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CHARACTERISTICS OF SOME TANGANYIKA SOILS

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WITH TWO PLATES

Summary

A series of soils from two areas of Tanganyika have been studied mineralogically. They are derived in the main from amphibolite, but only a small proportion of the more resistant aluminosilicate minerals survive in the soil. The clays ($< 1{\cdot}4\mu$) of the red loams are characterized by a predominance of kaolinite, whereas the more poorly drained grey soils have a disordered kaolin. Other components of the clays are iron oxides and small amounts of illite. The pallid soils contain moderate amounts of montmorillonite in the weathering zone, some of which persists into the soil. The mbuga and black valley soils contain montmorillonite or illite, with subordinate kaolin.

APART from Milne's accounts very little has been published on the soils of East Africa, and no studies of the mineralogy of the soils appear to have been carried out. The present research was undertaken to provide some fundamental information on soils on which the (British) Overseas Food Corporation has been endeavouring to develop a system of mechanized or partly mechanized farming. Two areas in Tanganyika were involved: Kongwa in the Central Province and Nachingwea in the Southern Province (see sketch map).

Kongwa. Situation and physical features, &c.

The township of Kongwa lies at an altitude of 3,300 ft. in Lat. 6° 12′ S. Long. 36° 25′ E. The area under development is a gently undulating plain, lying between 3,200 and 4,000 ft. above sea-level, with occasional inselbergs projecting above their surroundings. The underlying rock belongs to the Lower Basement Complex. A common constituent of this complex is a biotite-gneiss, described as migmatite by Temperley (1938). This alternates with belts of quartz-granulite, plagioclase-amphibolite, and metadolerite. The rock is exposed on the inselbergs and at a few small outcrops on the lesser hills and ridges. Elsewhere it is covered by a mantle of weathered material of local origin. At the crests of the ridges the mantle or pedisediment may be only a foot or two deep, but it increases in thickness down the slope and can attain a thickness of 20 ft. at the foot.

The annual rainfall (average over 5 years and several gauges) is 19·8 in., mostly falling in January, February, and March. There is a dry season of 7 months with, normally, no rain. The maximum temperature is about 95° F. and the minimum about 50° F.

On the footslopes of the hills of the Kiboriani range to the south of Kongwa, and of some of the larger inselbergs, shifting cultivation has produced a secondary bush very similar to that at Mpwapwa described by Greenaway (1933). Elsewhere there is a continuous blanket of

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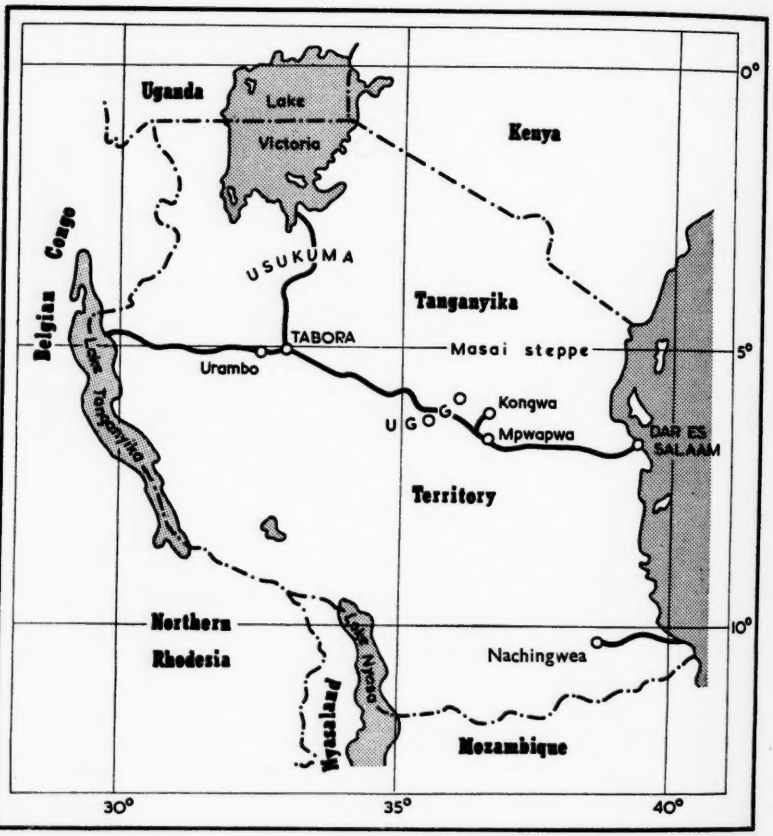
Commiphora thicket over all land except the seasonally waterlogged shallow depressions having the local name *mbugas*. The ground flora in the thicket is sparse. On the red soils baobabs are of frequent occurrence, but they are rare or absent on the pallid soils. The Commiphora thicket does not burn.



On the mbugas there is usually grassland with scattered trees and shrubs. The grasses are burnt annually by nomadic tribesmen. Locally, and probably associated with alkalinity or salinity in the soil, the grass is replaced by low shrubs such as *Croton menyhartii* Pax and *Salvadora persica* L.

The Soils. Typically the soils of the mantle are red in colour, but patches of pale grey or buff soils ('pallid soils') occur intermingled with the red. The following description is of a soil taken near the top of a slope under Commiphora thicket:

Profile 47. Chamaye (Red) sandy loam (analyses Table 1)

0–12 cm. Red-brown sandy loam (5 YR 4/6, dry). Top 5 cm. more friable than below. Merging into

12–105 cm. Red sandy clay (2·5 YR 4/8, dry). Massive; 12–35-cm. horizon harder than lower horizon. A few fragments of quartz, feldspar, and concretionary ironstone.

105–150 cm. (+) Quartz fragments and decomposing gneiss interspersed with red sandy clay (2·5 YR 4/8, dry, for the clay).

TABLE 1

Analyses of Fine-earth Fractions

Horizon (cm.)	*Fine earth as % of whole soil*	*Coarse sand* (%)	*Fine sand* (%)	*Silt* (%)	*Clay* (%)	*Moisture* (%)	*Organic carbon* (%)	pH	*Exchangeable cations (m.e./100 g.)* Ca	Mg	Mn	K	X
Profile 47. Chamaye sandy loam (red loam)													
0–12	Not det.	52·0	21·7	1·9	20·4	1·5	1·44	6·50	6·8	1·8	0·03	0·8	..
12–30	96·1	43·7	18·2	2·5	32·5	1·9	0·41	5·00	2·4	1·5	0·01	0·8	..
45–55	97·2	37·1	18·2	8·0	32·3	2·6	0·34	4·95	2·4	1·9	0·01	0·8	..
75–85	96·5	38·1	21·1	8·7	26·4	2·5	0·25	4·95	2·3	2·1	0·01	0·5	..
105–115	88·6	36·3	25·4	9·5	23·7	2·8	0·25	5·40	3·2	2·6	0·01	0·7	..
140–150	50·3	61·8	26·6	5·8	2·8	2·0	0·16	6·80	3·7	2·7	0·01	0·6	..
Profile 16. Nagaga sandy loam (lower-lying grey soil)													
0–7	100·0	42·2	39·0	2·9	12·3	1·2	1·25	6·60	4·5	1·8	0·15	0·37	7·6
7–17	99·7	38·8	41·5	2·8	15·3	1·0	0·68	6·30	2·4	1·0	0·17	0·27	5·2
17–30	..	..	..	..	..	..	0·36	5·25	0·5	2·1	0·04	0·25	6·0
30–45	98·3	44·9	16·3	1·3	34·8	1·8	..	5·10	..	..	..	..	..
65–90	94·4	42·4	13·2	2·4	39·8	2·0	0·23	5·20	0·3	1·8	0·00	0·25	6·2
125–150	82·4	45·9	15·0	3·7	33·5	1·9	0·13	5·20	0·3	2·0	0·00	0·15*	5·6
190–200	75·0	44·2	15·5	3·6	34·7	1·9	0·13	5·30	..	..	..	..	..

* +0·3 m.e. Na.

There were very few fibrous roots in the profile due to the very sparse ground flora, but tree roots reached to the full depth.

Towards the bottom of the slope the soils deepen considerably but the general appearance and colour remain the same. In the case of P. 2 (Table 6, below) no rock was encountered down to 235 cm. It seems that this group of soils could be referred to Kellogg's group of red latosols.

The 'pallid soils' mentioned above appear to correspond to the light-coloured 'plateau soils' of Milne *et al.* (1936). Similar soils, also described as 'plateau soils', are mentioned by Trapnell and Clothier (1937, p. 5) and Trapnell, Martin, and Allan (1947, p. 9 of memoir) as occurring in Northern Rhodesia. Later, however, Milne (1947, pp. 230 and 247) appears to have extended the term 'plateau soil' to include red earths with a concretionary ironstone horizon. The Kongwa 'pallid soils' also appear to correspond to some soils from NW. Tanganyika which Milne (ibid., p. 196) described as 'anomalous grey soils', and which occur in association with red earths, as do the Kongwa soils.

The following is an example of a pallid soil from Commiphora thicket with occasional baobabs and sparse ground flora:

Profile 3. Mtanana sandy loam (analyses Table 2)

0–10 cm. Yellowish-brown sandy loam (7·5 YR 5/6, dry). No fibrous roots; a few small tree roots, merging into

10–50 cm. Yellowish-red sandy clay (5 YR 5/8, dry). Massive structure. A few small roots.

50–65 cm. Band of subangular quartz stones.

65–85 cm. Pale reddish-yellow sandy clay (7·5 YR 6/6, dry).

85–110 cm. (+) Decomposing gneiss (7·5 YR 6/6, with white specks).

TABLE 2

Analyses of Fine-earth Fractions

Horizon (cm.)	*Fine earth as % of whole soil*	*Coarse sand (%)*	*Fine sand (%)*	*Silt (%)*	*Clay (%)*	*Moisture (%)*	*Organic carbon (%)*	pH	*Exchangeable cations (m.e./100 g.)* Ca	Mg	K
Profile 48. Nachingwea loam (red loam)											
0–20	99·7	38·2	27·8	2·9	26·3	1·6	1·43	5·95	4·9	4·4	0·4
20–60	97·9	23·0	13·0	2·1	58·5	2·4	0·85	5·50	2·5	3·2	0·2
60–100	88·2	17·8	14·0	8·7	55·9	2·3	0·48	5·95	2·8	2·9	0·1
105–160	67·9	27·4	17·5	8·2	44·7	2·3	0·21	6·65	3·1	2·1	0·2
Profile 49. Namatula loamy sand (upper-lying grey soil)											
0–12	98·9	72·0	17·7	1·5	6·6	0·7	..	6·90	3·9	2·0	0·4
12–40	97·3	73·3	17·4	1·6	6·6	0·5	..	5·80	1·0	1·4	0·3
40–64	95·3	62·8	15·8	2·3	17·2	0·9	..	5·20	0·8	1·6	0·3
70–130	50·5	46·5	19·5	5·0	25·5	2·3	..	5·65	0·9	2·5	0·6
Profile 3. Mtanana series (pallid soil)											
0–5	96·7	..	..	..	..	..	0·53	5·75	1·9	1·1	0·8
5–10	95·4	62·9	20·9	1·9	12·5	0·9	0·45	4·85	2·1	0·9	0·5
15–30	90·8	58·4	20·4	2·0	17·4	1·3	..	4·55	..	..	..
30–50	84·7	56·7	16·6	1·9	23·4	1·6	0·41	4·40	2·0	0·8	0·7
66–85	73·3	52·2	15·9	3·1	25·9	2·1	0·33	4·55	1·6	2·1	0·6

The present evidence suggests that these pallid soils form on similar mantle material to the red although in the above case the gneiss was more pegmatitic in character. Their somewhat pale colour seems due mainly to removal of iron from the soil under waterlogged conditions, or by long-continued leaching. In the western part of the area, which is drained by the river Kinyasungwe, the red soils predominate and the pallid soils, where present, are usually found on the crests of the ridges. Farther east the drainage has suffered from earth movements and the former valleys have silted up to form level mbugas. Here the pallid soils predominate, occupying the crests of all ridges and often extending all the way down the slope. In these circumstances it appears that red soils are formed only where denudation is active. Where denudation is slow there is time for the iron to be removed from the profile, sometimes to be deposited as concretionary ironstone just above the underlying rock, sometimes to be removed completely in the drainage water. An underlying layer of impervious rock, by causing temporary waterlogging, may be an accessory cause in the formation of these pallid soils but does not appear to be the main one.

The mbugas, mentioned above, may be several miles across and the alluvial filling 200–300 ft. thick. The following is an example of this type of soil under natural grassland with scattered thorn trees.

Profile 5. Lubiri loam (analyses Table 3)

0–10 cm. Dark grey loam (10 YR 4/1, dry). Friable, with many fibrous grass roots. Merging into

10–62 cm. Dark greyish-brown to brown loam (10 YR 4/2 at top, 10 YR 5/3 at base, dry). Fairly hard, massive structure, with a few fibrous roots.

62 cm. (+) Concretionary limestone.

TABLE 3

Analyses of Fine-earth Fractions

Horizon (cm.)	Fine earth as % of whole soil	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Moisture (%)	$CaCO_3$	Organic carbon (%)	pH	Exchangeable cations (m.e./100 g.)					Base exch. capacity (m.e./100 g.)
										Ca	Mg	Na	K	Mn	
Profile 5. Lubiri loam (dark grey mbuga soil)															
0–10	99·8	41·8	14·7	5·3	32·1	5·1	..	1·04	6·85	14·1	3·4	0·3	2·1	0·07	..
15–25	99·7	38·1	14·1	3·9	37·8	6·4	0·02	0·74	7·40	14·9	4·3	0·3	2·0	0·03	..
45–55	99·7	36·9	14·3	3·8	38·4	6·7	0·18	0·59	7·85	16·3	4·3	0·2	1·7	0·01	..
65–75	59·5	25·9	12·0	1·5	41·9	6·7	13·25	0·44	8·30	18·7	5·3	n.d.	1·6	n.d.	..
Profile 137. Naunga clay															
0–15	100·0	39·7	19·8	3·1	29·2	6·2	..	2·31	6·67	18·3	5·0	0·3	0·3	..	27·4
15–30	100·0	38·3	17·5	3·8	33·8	6·3	..	1·24	6·83	16·7	7·3	0·4	0·1	..	25·4
30–65	100·0	30·6	14·6	3·6	43·7	8·4	..	0·56	7·33	..	..	..	..	..	..
65–100	99·9	30·8	13·6	4·3	44·7	8·7	0·05	0·54	8·12	20·0	11·4	1·5	0·2	..	33·0
100–140	100·0	16·3	10·9	5·0	60·2	8·3	0·59	0·34	8·16	..	..	..	..	..	..
140–210	100·0	20·4	13·3	4·8	54·4	9·5	1·18	0·25	8·08	28·5	19·9	2·5	0·2	..	48·7

Nachingwea. Situation and physical features, &c.

Nachingwea is situated in the Southern Province (Lat. 10° 20′ S., Long. 38° 45′ E.) at a height of 1,500 ft. At Nachingwea itself, and for some miles to the west, the ground is gently undulating, with few hills. The country is considerably dissected with water-courses and there is evidence that it represents a former peneplain which has been elevated in geologically recent times, with resultant rejuvenation of the drainage. Namanga lies 4 miles to the north of Nachingwea and here, and also to the east of Nachingwea, there are several higher hills with exposed rock at their summits.

The annual rainfall is 33·7 in. (6-year average) mostly falling between mid-December and mid-April. Temperatures are a few degrees higher than at Kongwa and the humidity is also slightly higher.

The vegetation on soils with a sandy surface horizon is usually *miombo*, a deciduous woodland dominated by species of *Brachystegia* or *Pseudoberlina*. The ground flora is tall grass which is burnt annually in the dry season. Where the surface horizon is heavier there is usually a deciduous woodland of *Pterocarpus* sp. or *Ostryoderris* sp. associated with species of *Combretum* and tall grass or bamboo. This community is also swept by annual fires.

The Soils. The soils are all derived from Lower Basement Complex rocks, as at Kongwa. A dark amphibolite is a common constituent and a biotite gneiss outcrops fairly frequently. At Namanga, and in the eastern area, there are bands of quartz-granulite and of crystalline limestone. Near Nachingwea the higher ground is usually occupied by red loams or sandy loams, which have been named the Nachingwea series. (The word 'loams' is used in the sense that the feel of the soil when moist is similar to that of a loam from a temperate region. On drying, the soil becomes hard and massive. They probably can be considered as 'red latosols'.)

The soil represented by samples N. 27–29 (in Table 6) from 5 miles west of Nachingwea, is derived from amphibolite and it seems probable that this is true for the Nachingwea series generally. The following soil is another example from near Nachingwea under thin deciduous woodland with thick bamboo.

Profile 48. Nachingwea loam (analyses Table 2)

0–20 cm.	Dark brown loam (5 YR 3/3, dry). Friable, with weak crumb structure. Numerous fibrous roots (of bamboo?).
20–100 cm.	Dark red-brown sandy clay (2·5 YR 3/6, dry) with many coarse quartz grains. Hard and massive. Numerous fibrous roots throughout.
100–105 cm.	Line of subangular quartz stones (to 10 cm. diam.).
105–160 cm.	Dark red-brown sandy clay (2·5 YR 3/6, dry). Hard and massive, with much quartz gravel, ironstone, and MnO_2.
160–180 cm. (+)	Decomposing gneiss.

The level of the stone line and of the surface of the rotting rock undulates considerably.

Starting with these red soils a catenary succession of soils develops. Next down the slope is a brown or grey sandy loam with an orange

subsoil (Nagaga series) which in turn passes into a grey sand with an orange subsoil (Nailala series). Both of these can probably be considered as tending towards 'yellow latosols'.

The following description is representative of the former series under well-grown miombo woodland with grass 4 to 5 ft. high.

Profile 16. Nagaga sandy loam (analyses Table 1)

0–7 cm.	Dark brown sandy loam (7·5 YR 4/2, dry) single grain structure. Many fibrous roots.
7–17 cm.	Brown sandy loam (7·5 YR 4/3, dry). Similar to above, merging into
17–30 cm.	Reddish-brown sandy clay (2·5 YR, 4/5, dry). Harder than above, becoming massive. Fewer fibrous roots.
30–90 cm.	Yellowish-red sandy clay (5 YR 5/6, dry). Massive, harder in upper layers than below perhaps because of drying out of upper layers. A few fibrous roots to 60 cm. depth.
90–150 cm.	Reddish-yellow clayey sand (5 YR 6/8, dry) with soft ferruginous concretions.
150–190 cm.	Yellow-brown clayey sand with red-brown, yellow, and white mottling. Some larger roots.
190–220 cm. (+)	Red-brown, yellow, and white mottled indurated clayey sand. Some earthy ironstone with MnO_2, rotten feldspar, and quartz gravel, i.e. decomposing gneiss.

Below these two series come sands with a clayey subsoil, i.e. with impeded drainage, and, finally, a range of grey or black loams and clays. In a few places to the west of Nachingwea, the Nachingwea red loam is replaced by shallow, sandier soils, brown or grey at the surface and with a yellowish-brown or light reddish-brown subsoil. These soils, from their frequent position on ridges and from the pattern of their occurrence —elongated strips parallel to the strike of the gneiss—appear to be associated with the outcrop of a parent rock different from that of the red soils. They are referred to in Table 6 (below) as 'upper-lying grey soils'. The biotite-gneiss often outcrops near areas of this soil. Samples N. 24–26 (reported in Table 6) from near N. 27–29, represents one of these soils derived from a pegmatite. Profile 49, Namatula series, from near profile 48, is probably another of this group, though the parent rock was not visible. This series is represented in the following description. The vegetation consists of thin miombo woodland, but trees individually are well grown. Grass 5 to 6 ft. high. Termite mounds are common.

Profile 49. Namatula loamy sand (analyses Table 2)

0–12 cm.	Dark grey loamy sand (10 YR 3/1, dry). Fairly friable, with many fibrous roots.
12–40 cm.	Pale brown loamy sand (10 YR 6/3, dry). Moderately hard and massive, but with some fibrous roots throughout.
40–64 cm.	Light yellow-brown very sandy clay (10 YR 6/4, dry), with pea-sized ironstone concretions. Moderately hard and massive.
64–70 cm.	Line of subangular quartz stones.
70–140 cm. (+)	Massive concretionary ironstone, slag-like.

Lower down the slope these soils give rise to a catena of sands, impeded sands and clays, not very different from the lower part of the

Nachingwea catena, though the width of the sand belt tends to be increased.

Around Namanga the individual soils do not differ appreciably from those at Nachingwea, but their proportions are different. The Nagaga sandy loams and sands and the valley loams and clays are more extensively developed, while the Nailala sands are reduced to narrow strips. This may be due to differences in the parent rock, but is more likely to be an effect of the hillier topography and the longer slopes on catena development. The mantle of weathered rock also tends to be deeper here, so that none of the profile pits reached rock at 6 ft. On Namanga hill itself there are outcrops of quartz-granulite and limestone.

Associated with the Nachingwea group of soils in this area is a black clay of the Naunga series which appears to have been developed on finer material brought down a water-course. It would appear, therefore, to have come from the same parent rock as the red soils higher up the slope, but to have developed under conditions of poor internal drainage. In this it would seem to correspond to van der Merwe's (1941) 'Subtropical Black Clays' better than many of the other mbuga soils in Tanganyika. Petrographic analyses of the rocks of the adjoining slopes showed that they were typical basement complex rocks. The following description exemplifies this series. Although the ground in the neighbourhood of the profile has a slope of about 1½ per cent., the profile is situated at the intersection of two shallow drainage-lines and so will receive a considerable amount of surface flood water after heavy rains.

Profile 137. Naunga sandy clay

Under natural grass, about 3 ft. high, with scattered trees and shrubs (analyses Table 3).

0–15 cm.	Black sandy clay (2/0, dry), with weak angular blocky structure. Wide cracks (up to 4 cm.) on drying. Many fibrous roots. Merging into
15–30 cm.	Black clay (5 YR 2/1, dry). Similar to above but few fibrous roots. Merging into
30–65 cm.	Dark grey clay (4/0, dry) with brown mottling. Weak angular blocky structure. Cracking widely on drying. A few fibrous roots. Merging into
65–140 cm.	Dark grey clay (4/0, dry), hard and massive. Cracking on drying. A few roots. Occasional carbonate concretions; a little concretionary ironstone (up to 3 mm.) with MnO_2. Sharply defined, over most of profile face, by a slightly undulating layer of petrified strap-like tree roots, from
140–210 cm.	Grey clay (3/0, dry), cloddy. Irregular vertical and horizontal cracks spaced at about 10-cm. intervals. A few carbonate concretions.

The petrified tree roots, mentioned above, while retaining their original shape had largely been converted into iron oxide. The reason for their concentration in one horizon is not at all clear but is perhaps due to seasonal waterlogging, the increase in sodium ions or some similar adverse condition, in the horizons below.

Analyses of the Soils

Tables 1 to 3 give analyses of the fine earth fraction (< 2 mm.) of the samples. Organic carbon was determined by the Walkley and

Black method, and calculated on the basis of an 80 per cent. recovery. pH values were obtained using a glass electrode at 1:2·5 soil/water ratio. The exchangeable cations were estimated in a neutral ammonium acetate extract. The magnesium was determined in some cases colorimetrically using Titan Yellow, a method giving only approximate results.

The trend in pH values resembles that of some red-yellow and of most grey-brown podzolic soils, with a pronounced minimum in the middle layers, which is especially evident in those profiles in which bedrock was reached, e.g. P. 47 (cf. Kellogg and Davol, 1949). Here the pH of the weathering rock material is about 7. In the grey mbuga soil (P. 5) the pH is high throughout as would be expected. The exchangeable cation values present no remarkable features apart from the relatively high values for magnesium which is probably due to the hornblendic rocks.

As shown by the mechanical analyses there is generally a tendency to clay accumulation in the middle horizon of the soils, but the apparent decrease in clay content in the lower layers is in many cases due to cementation by iron oxides. The clay content of the surface soils is in general low, and the silt content characteristically low throughout.

Mineralogy of the Parent Rocks

One of the main types of rock giving rise to the mantle of debris from which the soils are derived is a gneiss or amphibolite rich in hornblende, with quartz-feldspar segregations and pegmatites. A sample of the rock from 5 miles west of Nachingwea (N. 29) had the following modal composition:

hornblende	69·5	scapolite	9·0
diopside	7·0	rutile	0·5
quartz	2·5	magnetite	
andesine	11·5	apatite	

This rock appears to correspond closely with the plagioclase-amphibolite described by Temperley (1938) as occurring in the Kongwa area. In another specimen (from the base of P. 47) there was present a small amount of biotite. An examination of one of the pegmatite veins that occur locally showed that it consisted mainly of coarse-grained microcline with local concentrations of brown biotite. Quartz was present to the extent of about 5 per cent.

Pieces of the weathering biotite-gneiss from under the shallower red soils (e.g. P. 47) were still moderately fresh, although stained rusty brown. The feldspar was partly clouded; the biotite was weathering yellowish, probably to hydrobiotite, but still gave a good optical figure; the hornblende was only slightly weathered. Under the pallid soils, however, there appeared to be a marked difference in the course of weathering. Pieces of weathering rock of pegmatitic nature from the base of P. 3 had a white patina on the outside, due mainly to quartz, while the core was rusty stained with some relatively fresh hornblende and feldspar. The change is a fairly sharp one with an intermediate yellowish layer from which the ferromagnesians have nearly all disappeared. It would seem that a reduction and dissolution of iron must

take place fairly rapidly, the iron migrating, partly to the valleys and partly being deposited in the concretionary horizon of the soil (see also below, p. 14).

Mineralogy of the Sand Fractions

The fraction studied in detail was the international fine sand (0·2–0·02 mm.). The sands from the surface layers of the soils were remarkably clean and required no acid treatment. On the other hand, the sands from the basal layers, even from the mottled horizons, were heavily stained with iron oxides, and required treatment with *N*–HCl to render them clean enough for optical examination. Two fractions were separated using bromoform (s.g. 2·86), and the percentages of light and heavy minerals determined. The relative amounts of the mineral-species were determined by microscopic counts which were facilitated by the use of a mechanical stage. The distribution of minerals in the fine sands is shown in Table 4.

TABLE 4

Mineralogy of the Fine-sand Fractions

	Chamaye red loam P. 47	*Nachingwea red loam P. 48*		*Namatula grey sandy loam P. 49*	*Nachingwea red loam P. 17*		*Nagaga sandy loam P. 16*	
Soil and depth	0–12 cm.	0–20 cm.	100–160 cm.	0–12 cm.	0–10 cm.	100–150 cm.	0–10 cm.	175–220 cm.
Light minerals	96	94·8	93·4	97·2	94·6	97·4	98·7	93·4
Feldspars .	20	0	9·5†	5·5	0	0	11	4·5†
Quartz . .	76	94·8	83·9	91·7	94·6	97·4	87·7	88·9
Heavy minerals*	4	5·2	6·6	2·8	5·4	2·6	1·3	6·6
Grains counted	368	612	536	488	532	1,003	1,037	371
Hornblende .	52·4	53·1	88·0	52·5	16·0	1·1	5·3	1·5
Black Iron Ore	30·9	29·9	4·1	28·9	71·0	89·5	58·2	54·2
Kyanite .	6·0	4·7	..	1·5	1·4	0·8	4·3	2·9
Almandine .	1·4	2·3	8·1	0·6	1·9	0·5	..	0·4
Zircon . .	1·4	5·4	1·0	9·4	2·6	3·6	9·9	9·2
Rutile . .	1·6	1·6	..	2·0	0·4	0·9	1·2	1·8
Epidote . .	5·4	1·0	..	1·8	0·6	0·3	..	..
Staurolite .	1·6	0·6	..	0·6	1·7	1·2	2·5	2·9
Sillimanite .	..	0·5	..	2·6	4·4	2·4	18·9	26·2

* Fraction as % of fine sand; minerals as % of fraction.
† Decomposed.

In general the 'light fraction' (s.g. $< 2{\cdot}86$) consisted of quartz with a varying admixture of feldspar which was sometimes partly decomposed. In the profiles from 5 miles west of Nachingwea (N. 27–29) the scapolite present in the rock had disappeared completely even from the basal soil layer.

The 'heavy fraction' (s.g. $> 2{\cdot}86$) was made up principally of those minerals normally developed in metamorphic rocks of the gneissose type. The species noted include the following: amphibole, iron ores, garnet, kyanite, sillimanite, zircon, rutile, epidote, and staurolite. Small amounts of tourmaline and biotite were also present, but so sporadically that no significance could be assigned to them. Their occurrences are noted in the descriptions of the heavy mineral varieties that follow.

The *amphibole* is a dark green hornblende forming elongate 'platy' cleavage flakes with a vitreous lustre.

Iron ores. These vary from rounded to subhedral grains, often in the same

separate. Indications are that most of the ore is magnetite (easily separated with a hand magnet); no leucoxene observed.

Garnet. A pink garnet varied considerably in quantity, but generally exhibited similar characteristics throughout: irregular to subrounded: even in surface layers the rounding process is incomplete. The surface of the grains is somewhat pitted and rough suggesting the beginning of weathering.

Kyanite. The quantity and quality of this mineral is a feature of the sands. It generally occurs in typical 'bladed' crystals with irregular terminations. Inclusions are uncommon.

Sillimanite. This occurs as prismatic grains, often slender, sometimes flattened, and showing some 'splitting' lengthwise. They often bear a superficial similarity to the kyanite, as they are less elongate than is usual for this mineral.

Zircon. A typical variety showing a good degree of roundness; prismatic grains are commonest, although some 'stumpy' grains are present. Inclusions are fairly common.

Rutile. Red, yellow, and amber coloured grains; some prismatic, but more commonly rounded.

Epidote. This mineral is characterized by its distinctive pleochroism from yellowish-green to colourless. Generally the grains are irregular, angular, and have a 'hackly' surface.

Staurolite. Generally occurs in poorly developed prismatic grains, brown and yellow in colour.

Tourmaline. A dark brown, very strongly pleochroic variety was noted in P. 16 and P. 17 in very minor amounts.

Biotite. In the sands of P. 16 a biotite of medium-brown colour was found in small quantity.

Although specimens of the underlying rock have been available only from one or two of the profiles, the soils from Kongwa and Nachingwea would appear to have been derived from rocks of approximately the same composition, namely the amphibolites described above. In contrast, the two soils from Namanga (P. 16 and 17), in particular the lower-lying grey soil (P. 16), appear to have been formed largely from the weathering products of a gneiss containing a fair amount of sillimanite. The ferromagnesian minerals show a low stability to weathering, and it is only in the vicinity of the weathering rock, or when the soils are shallow, that an appreciable amount of these minerals are present. Even in the basal layer of P. 48 and N. 27–28, where the samples are from near the rock, the ferromagnesians have decreased from about 70 per cent. in the rock to about 5 per cent. in the soil. The diopside in the amphibolite of a red soil profile N. 27–29 has disappeared completely in the soil and the hornblende has been reduced to 2–3 per cent. The latter, however, usually forms the main part of the 'heavy fraction' of the red soils. The iron ore is present in large amounts and may form nearly 90 per cent. of the 'heavies'. The somewhat wide variations in the hornblende and iron ore percentages do not necessarily have much significance, as the gneisses are not homogeneous even over a small area.

Composition of the Clay Fraction

The amounts of the clay fractions ($< 2\,\mu$ and $< 1\,\mu$) separated in the course of mechanical analysis (Table 5) indicate that the clay is in general below $1\,\mu$ e.s.d. and this is borne out by the electron micrographs of

TABLE 5

Composition of Clay Fraction as percentage of Ignited Clay

Method of dispersion	*Profile 3. Pallid soil*			*Profile 47. Red loam*				*Profile 5. Lubiri loam*	
	International			*Puri*				*International*	
Horizon	*0–10 cm.*†		*30–50 cm.**	*0–10 cm.*†		*45–55 cm.*†		*0–10 cm.**	*45–55 cm.**
Particle size	$< 1\mu$	$1–2\mu$	$< 1\mu$	$< 1\mu$	$1–2\mu$	$< 1\mu$	$1–2\mu$	$< 1\mu$	$< 1\mu$
% of total clay ($< 2\mu$)	*95·5*	*4·5*	*98·4*	*81·7*	*18·3*	*91·2*	*8·8*	*95·5*	*96·6*
SiO_2	50·2	59·3	51·7	46·7	47·3	47·9	47·9	58·2	57·7
Al_2O_3	34·6	20·4	39·3	35·6	34·4	36·4	34·8	26·8	28·1
Fe_2O_3	9·9	10·6	7·9	12·8	13·5	11·6	12·3	7·3	7·3
TiO_2	1·5	2·1	1·17	1·4	1·6	1·1	1·4	1·15	1·22
P_2O_5	0·4	0·3	n.d.	0·3	0·3	0·2	0·2	not determined	
CaO	0·02	trace	0·01	0·02	0·01	nil	nil	0·50	0·59
MgO	0·68	0·33	0·49	0·58	0·63	0·50	0·7	1·93	1·96
Mn_2O_3	0·03	0·03	0·02	trace	trace	trace	trace	0·051	0·065
K_2O	not determined		1·14	not determined				3·0	3·0
Na_2O	„	„	< 0·3	„	„			< 0·3	< 0·3
Molecular ratios									
SiO_2/Al_2O_3	2·47	4·96	2·24	2·28	2·35	2·24	2·34	3·68	3·52
SiO_2/R_2O_3	2·09	3·72	1·98	1·81	1·87	1·86	1·91	3·14	2·99
Al_2O_3/Fe_2O_3	5·49	3·01	7·81	4·36	3·99	4·93	4·45	5·77	6·03

* Analysis by C. L. Bascomb and H. H. Le Riche. † Analysis by B. Anderson.

Plate I. From these pictures it is evident that the majority of the platy crystallites are about 0·1 μ in diameter. The chemical composition of selected clay samples is given in Table 5.

There is little change in the composition of the clay fraction within each profile, although some differences will be noted, and it appears that each of the main soil groups described above can be characterized by the clay minerals present. This is shown in Table 6 which is based on X-ray analysis.

TABLE 6

Composition of Soil Clays

	Kaolinite	*Fire-clay mineral (Disordered Kaolin)*	*Illite*	*Montmorillonite*	*(Hydrous) iron oxides*
1. Red Loams:					
P. 2	+	..	[+]	..	+
P. 47	+	..	(+)	..	+
P. 17	+	..	[+]	..	+
P. 48	+	..	(+)	..	+
N. 27–29	+	..	(+)	..	+
2. Pallid Soil:					
P. 3	(?)	+	+	..	(+)
3. Upper-Lying Grey Soils:					
P. 49	(+)	+	..	..	..
N. 24–25	+	(+)	+	..	..
4. Low-Lying Grey Soil:					
P. 16	..	+	..	..	..
5. Black Soils:					
P. 137	+	..	..	+	..
P. 5	(+)	..	+	..	..

\+ Dominant or in moderate amount. (+) Present in small amount.
[+] Probably present. (?) Doubtfully present.

The red loams have a fine-grained kaolinite as the dominant mineral, associated with some haematite (up to 10 per cent.) and occasionally minor amounts of goethite and illite. The pallid and grey soils contain an illite, in addition to a kaolin, in moderate amounts and also a little haematite and some quartz. P. 3, an upland pallid soil, contains some halloysitic material as can be seen from the electron micrograph (Plate II A), and there is also a mineral giving a diffraction line at about 13·8 Å. The grey soils of the lower position in the catena at Nachingwea show a kaolin, a small amount of illite, and no iron oxides. The dark grey mbuga soil (P. 5) from Kongwa contained a dioctrahedral illite with a little kaolin. The black valley soil from Nachingwea (P. 137), which is essentially non-calcareous, showed a montmorillonoid with some 20–30 per cent. kaolin. The montmorillonoid belonged to the intermediate montmorillonite-beidellite group.

It has been possible to get an idea of the initial stages of weathering of the gneisses from the examination of clay separated from the pieces of weathering rock described above: one from under a red loam (near

P. 2) and the other from the base of the pallid soil (P. 3). The results are shown in Table 7.

TABLE 7

Clay Minerals from Weathering Rocks

Clay minerals	*Under red loam*	*Under pallid soil*
Montmorillonoid .	trace	+
Mica . . .	+	++
Kaolin . . .	+++	+
Goethite . .	(+)	(+)
Haematite . .	(+)	(+)
Anatase . .	trace	trace
Gibbsite . .	?	..
Quartz . . .	..	trace
Feldspar . .	..	present

In the case of the red loam it is evident that the primary rock minerals, e.g. ferromagnesians and feldspars, weather in the main straight to kaolinite, mica, and iron oxides. The evidence for gibbsite is doubtful and the amount present can only be quite small. There is no trace of boehmite. It may be that the apparent absence of basic feldspars precludes the occurrence of hydrous aluminium oxides in any quantity.

The contrast of the course of weathering under the pallid soil is quite striking, the amount of montmorillonite in this case possibly being of the order of 20–30 per cent., the mica content likewise being much higher. Milne (1947, p. 196) suggested in connexion with the 'anomalous grey soils' that 'petrographic examination may reveal a mineral composition that would direct the course of weathering towards the production of a water-retentive "fat" clay. . . .' The difference between the fresh rock materials in the present two cases is not such as to suggest that montmorillonite would form preferentially in the pallid soil and it must be assumed that the cause is the sluggish drainage as suggested earlier for the difference in morphology. This result may be compared with those obtained by Nye (1955) in his study of a Nigerian catenary sequence.

While there is no trace at all of montmorillonite even in the lowest soil layers of the red loams, a small amount probably persists in the pallid soil (P. 3), although the chemical analysis does not suggest that there can be much. Mica is, however, quite a prominent constituent even in the surface layer of this profile. This mineral is most prominent in the soil (N. 24–25) overlying the rock with most feldspar, and it is probable that the latter is the source of the illite constituents with the necessary magnesium and iron coming from the ferromagnesians present. The clay from the lowest layer of this soil, i.e. adjoining the rock, gave somewhat broader diffraction lines than the clay from the topsoil, suggesting an improvement in crystallinity in the surface layers.

Although the clays from the surface and lowest layers of the pallid soil (P. 3) also showed this difference in diffraction pattern to a slight extent, the electron micrograph (Plate II A) and the X-ray diagram show that the clay does not appear to be particularly well crystallized

even in the surface layer. The shapes of the particles are rather indefinite and few hexagons are to be seen. The rather 'sooty' appearance of this clay is presumably due to carbonaceous matter since drastic treatment with boiling hydrogen peroxide cleaned it up fairly well. The majority of the red and grey soil clays gave electron micrographs like that of Plate I A, indicating, apparently, a well-crystallized mineral. In these photographs the kaolin particles appear to be co-sedimented in preparation with larger platelets (Plate I B). The degree of orientation of the small plates on the large is marked, but whether or not there is any genetic connexion between them is not known. The larger particles are assumed to be illite since they are commoner in the clays showing most of that constituent, but it has proved impossible to separate them for positive identification. They may, of course, in part represent strongly cemented aggregates or intergrowths of the smaller particles.

In spite of the general similarity of all the kaolins under the electron microscope the X-ray diffraction diagrams show that they can be differentiated into kaolinite and the disordered kaolin (Pugu D) of Robertson, Brindley, and Mackenzie (1954) by the band at 4·47 tailing off to higher angles (Plate II B). The well-drained soils (e.g. N. 27, &c.) appear to consist largely of kaolinite, whereas those with evidence of poor drainage (e.g. P. 16, &c.) contain predominantly a disordered kaolin. The white mottles in the lower layers of P. 16 give an apparently very pure specimen of this variety. It is evident that although such a difference may be reflected in the electron micrographs as shown by Robertson *et al.*, this need not be the case. The fact that in the present instance the grey lower-lying soils (P. 16) seem generally to contain the disordered kaolin may have a bearing on the origin of the Pugu D material which is described by these workers as a marine deposit. It is likely that in normal erosion the lower position soils would contribute a considerable proportion of the clay carried by streams to the sea on account of the more frequent flooding that they experience and thus contribute to the accumulation of a disordered kaolin deposit.

Differential thermal analysis of a selection of the clays gave curves corresponding to the minerals identified by X-rays, except for the illite in the pallid soil, P. 3, which did not register on the thermal diagram, presumably due to its lower sensitivity. The red and pallid soils give a thermogram approximating to that of a kaolin, with a slight skewness on the 600° peak possibly due to the small particle size. A broad exothermic peak about 400° seems due to sesquioxides and organic matter for it disappears after hydrosulphite treatment of the clay. In none of the thermal analyses made was any sign of gibbsite or boehmite noted, nor did these show up on the X-ray diagrams. The illite of the grey calcareous mbuga soil (P. 5) gives a fairly characteristic thermogram with a high moisture peak.

For an examination of the chemical composition of the clay two fractions, viz. $1-2\,\mu$ and $< 1\,\mu$ e.s.d. were separated in some cases by repeated decantation after pretreatment by the International method for mechanical analysis and the Puri carbonate method (Puri, 1935); the latter did not appear to give complete dispersion.

The analyses given in Table 5 show that the coarser clay fraction (1—2 μ) contains more silica than the fine clay. This is almost certainly due to admixture of quartz, for this forms the main constituent of most of the silts and extends down into the coarser clay. The X-ray results described above, which were obtained on clay that would be less than 1·4 μ e.s.d., show very little quartz. In general the molecular ratios for the red clays agree with the mineralogical results, i.e. the silica-alumina ratios are in general close to 2. The clays are thus essentially kaolins, with more or less illite and iron oxides, but with no suggestion of any appreciable amount of free alumina. Even in the case of P. 17 (0–10 cm.), the clay of which has a silica/alumina ratio of 1·59, no evidence for crystalline hydrous aluminium oxides was obtained.

Discussion

The profiles described above are typical of large areas of soils over basement-complex rocks in Tanganyika and probably elsewhere in Africa. The examples examined form catenary sequences from the shallow red loams and pallid soils on the upper slopes and ridges, through the deeper red loams of the middle slopes to the grey soils of the lower slopes and the dark grey clays of the mbugas. The parent rock, while in general an amphibolite, varies sufficiently locally to be reflected in the appearance of some of the shallower soils. In the main, however, since the soils are formed on a mantle, or pedisediment, there has been much mixing of the weathered products and it is only by an examination of the resistant heavy minerals that an indication of the probable source rocks is obtained.

The sand mineralogy shows that in the main the soils have reached a late stage in the weathering cycle in that only minor amounts of the more complex silicates occur, in particular the feldspars, except where they are shallow (e.g. P. 47). In two cases the feldspar, although present in moderate amount, was highly decomposed. Of the heavy minerals hornblende, as might be expected, is the dominant silicate although other more resistant minerals may sometimes be abundant, e.g. sillimanite.

From the rock specimens examined the rate of decomposition of the primary minerals is evidently fairly rapid; at short distances from the rock the more readily decomposable substances, e.g. scapolite, have completely disappeared, and even hornblende is reduced to quite small amounts. This is particularly marked in the case of the pallid soil P. 3 (above, p. 3). The advance of the 'weathering front', i.e. the zone of penetration of water and air into the rock, appears, however, to be very slow.

It has not been possible to follow in detail the alteration of the various weathering minerals, although biotite apparently goes through a hydrobiotite stage in breaking down. The other minerals presumably provide the illite and the dominant kaolins, together with the iron oxides. Illite appears to persist in variable, but generally small amounts into the surface soils even in the deeper mantle material. In the initial weather-

ing of the parent rocks, even under the red loams, small amounts of a montmorillonoid are formed, but rapidly disappear. Under the pallid soil, however, a montmorillonoid is formed in moderate amounts and persists in the soil to some extent. This difference from the red soils must be ascribed to the poorer drainage in the pallid soil. Little information seems to have been published on the clay mineralogy of soils from rocks comparable with the Kongwa amphibolites. For the Piedmont region of the United States Alexander, Hendricks, and Faust (1942) have shown that somewhat more feldspathic (andesine) amphibolites than ours can give rise to kaolin and gibbsite in the Davidson soil series, the latter mineral persisting into the surface soil. The scapolite in the Kongwa rocks could, however, be considered simply as a more readily decomposable feldspar and thus expected to produce gibbsite if the other conditions were favourable, which apparently they were not. Why this is so is not at all clear. It could, of course, be that the rainfall is inadequate, following the relationship shown by Van der Merwe and Heystek (1952) for South African soils. There, apparently, little or no gibbsite occurred if the annual rainfall was less than about 30 in.

Although it has been pointed out above that the disordered kaolin is more characteristic of the poorly drained soils (excluding mbugas) and kaolinite of the well-drained red loams, it is not suggested that this is generally true, for not enough evidence is yet available.

In the case of the mbuga and black valley soils, it is evident that they are influenced to some extent by their 'parent material'. In general it seems that, if they represent the lowest point of pedisedimentation, they are probably characterized by the dominance of a montmorillonoid in the clay fraction (e.g. P. 137). If, on the other hand, as seems fairly common in parts of East Africa, they are derived from old lake sediments, they inherit the clay minerals characteristic of the sediment (e.g. P. 5, above).

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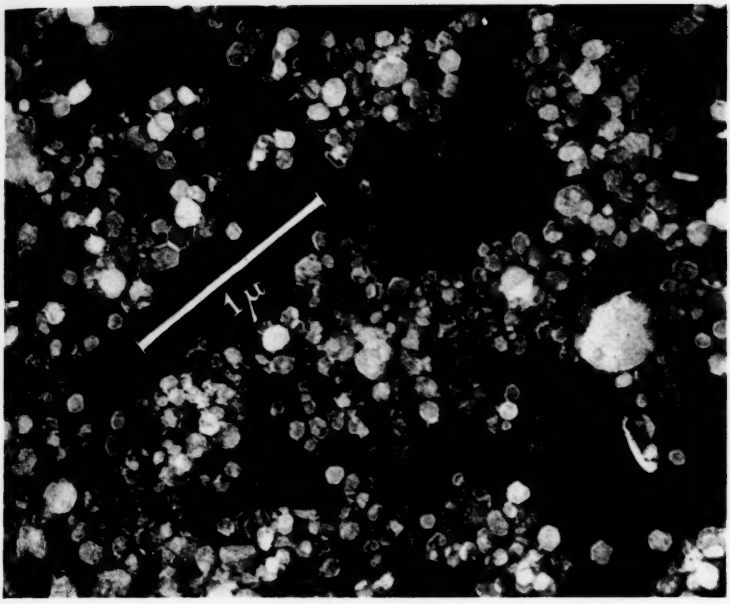
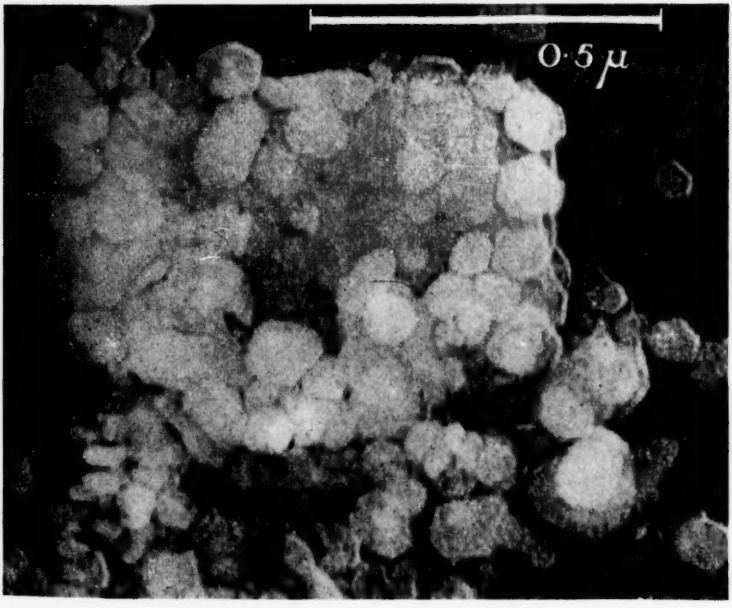
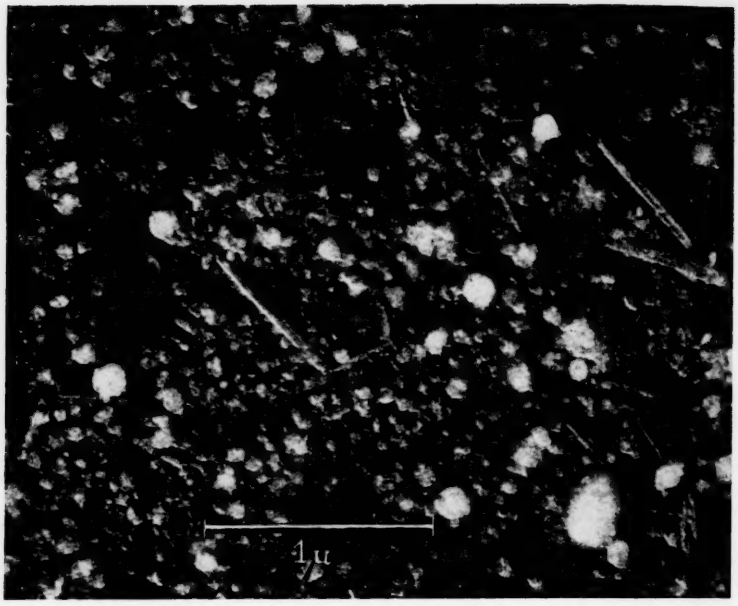


I A. Kaolinite from red loam soil (P. 48)

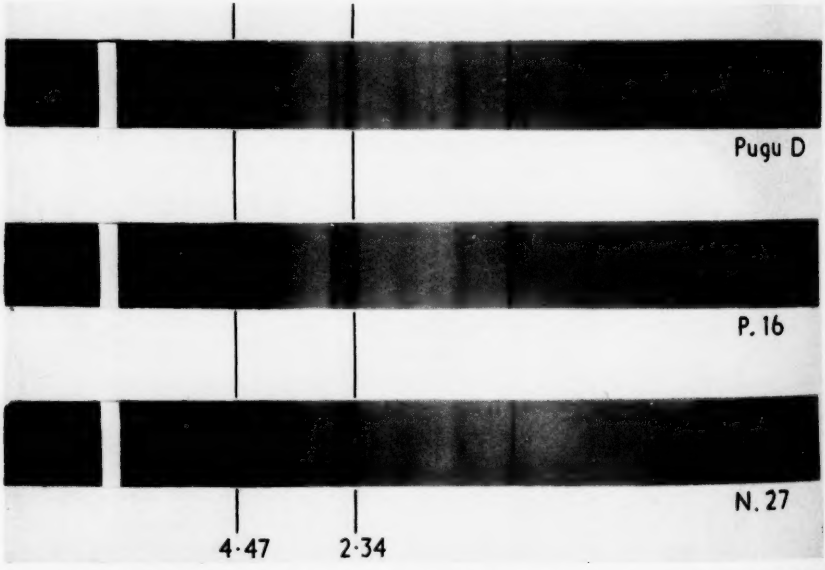


I B. Enlargement of aggregate of mica (?) and kaolinite (P. 48)

A. MUIR, B. ANDERSON, AND I. STEPHEN—PLATE I



II A. Clay from pallid soil (P. 3) showing halloysite rods with illite and kaolin



II B. X-ray photographs of soil clays showing mainly disordered kaolin (P. 16) and kaolinite (N. 27), with specimen of Pugu D for comparison. Particle size in P. 16 and N. 27 *ca.* 0·1–0·2 μ, in Pugu D, $< 2\,\mu$

THE MICROPEDOLOGY OF SOME RED SOILS FROM CYPRUS

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WITH ONE PLATE

Summary

The micromorphology and mineralogy of terra rossas and rotlehms associated with calcareous sediments and igneous rock material respectively are described. The investigations confirm differences observed in the field and assist in the differentiation and classification of the soils.

EXCEPT for the descriptions and data given by Reifenberg and Ewbank (1933 *a*, *b*) and some general accounts by geologists and others, little has been published about the soils of Cyprus. It is a suitable place to study the development of soils on calcareous sediments under a Mediterranean climate for it mainly consists of such sediments which, except on the western side, surround an elevated mass of basic igneous rocks.

Much of the island is covered by red-coloured soils associated with Pleistocene deposits which are extensive in the plain around Nicosia and extend towards Famagusta and Larnaca. Similar soils occur on the hard, massive, grey limestones of the Kyrenia Mountains along the north coast. Reddish-coloured soils are also found in parts of the igneous rock mass, particularly in its foothills on colluvial and alluvial deposits mainly derived from it. Except locally, where a red-coloured chalk forms the parent material, no red soils are found on the white Lapithos chalk the soils of which can be classed as rendzinas. During a visit to Cyprus by one of the authors (D. A. O.) it was observed that the red soils associated with the various calcareous sediments differed among themselves and from those on the igneous rocks. Samples were therefore collected from representative sites for study.

Experimental

In order to preserve the natural structure of the soils, the samples were collected using the frame technique (Kubiena, 1954). Subsequently blocks were impregnated with a synthetic resin (Ceemar embedding resin) and thin sections, about 30μ thick, were prepared for optical examination by the normal procedure except that grinding was done entirely dry with carborundum powder (100 and 220 mesh) and finally with 'aloxite fine H'. The sands were examined optically after separation into 'light' and 'heavy' fractions using bromoform (s.g. 2·85) and the clay fractions were investigated by X-ray analysis.

I. *Soils on Calcareous Parent Material*

The 'terra rossa from chalk pan' described by Reifenberg and Ewbank is presumably the soil commonly found on some of the Pleistocene deposits which, locally, are called 'kafkalla', 'havara', or simply

'crust'. The deposits consist of 8–10 ft. of white, incoherent, highly calcareous marl (havara) with small fragments and mineral grains from igneous rocks that overlie parts of the Miocene beds and the conglomerate. As the surface of the havara is approached it becomes more porous but harder until, at the surface, there is a layer of hard limestone

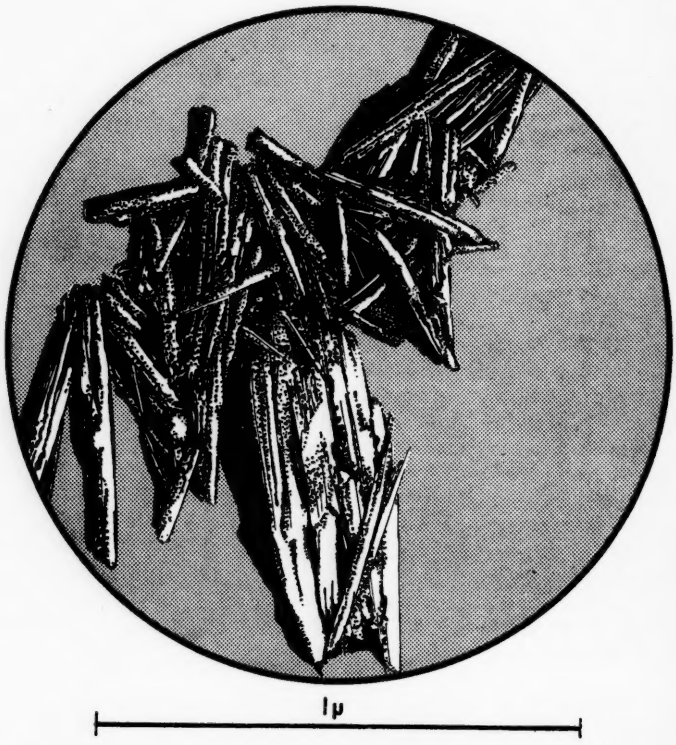

FIG. 1. Palygorskite from kafkalla.

varying in thickness from ¼ to 1 in. with narrow alternating cream and reddish-coloured bands. Large bare surfaces of this limestone are called 'kafkalla' and its surface is often studded with igneous boulders, gravel, and sand grains or, where it occurs near the Kyrenia Mountains, with dark coloured Hilarion limestone pebbles.

An optical study of the coarser material (> 0·05 mm.) of the 'insoluble residue'* from the kafkalla showed the presence of the following minerals: quartz, opaline silica, feldspars (mainly non-calcic varieties),

* The kafkalla and the (B) horizon of the soil above it were treated with ammonium acetate at pH 3 in order to remove calcium carbonate before separation of the sands and clays.

epidote, magnetite, amphiboles, and zircon with small amounts of pyroxenes, garnet, and apatite. The opaline silica occurs as irregular and angular fragments, normally isotropic, but some grains exhibit very weak polarization and show a vague interference cross of negative character between crossed polars. X-ray analysis of the clay fraction shows the presence of moderate amounts of mica, kaolin, and palygorskite with accessory quartz, goethite, and anatase. An electron micrograph of the clay (Fig. 1) shows the palygorskite to occur as laths, both singly and in bundles, the individuals ranging up to 0·8 μ in length and being 5–30 mμ wide.

Where the hardened havara is exposed, very pale yellowish-grey or brownish-grey rendzinas are found, but the kafkalla is more generally associated with red or brownish-red, more or less calcareous clay soils varying from about 6 in. thick to 3 ft. in shallow depressions. Samples of the A and (B) horizons were taken from a profile about 2 miles north of Kokkini Trimithia at about 700 ft. O.D. on a very gently inclined plateau. When dry the colour of the A horizon is dark red (2·5 YR 3/6), and that of the (B) is red (2·5 YR 5/6). Calcium carbonate is present mainly as limestone fragments and increases from 12 per cent. in the A horizon to 23 per cent. in the (B) horizon at 9–11 in. The clay content is practically constant at about 34 per cent. throughout the profile and the soil is friable and easily worked when dry. The structure is granular throughout and although compaction increases with depth, the (B) horizon can be crumbled when dry.

The (B) horizon rests directly on the kafkalla and the debris preparation showed the fabric to be intertextic (Kubiena, 1938) with a dull, porous, and granular appearance. In thin section (Plate I *a*) the reddish-brown groundmass is flocculated, has many cavities and fine sinuous cracks, and there is a tendency to form rounded aggregates displaying the Iwatoka phenomenon (Kubiena, 1948). There are no doubly refracting streaks indicative of clay movement, nor is there any coating of the grains. Calcite is abundant as fragments of finely crystalline limestone that in many instances have been replaced by the groundmass so that their shape can only be determined between crossed polars. Igneous rock fragments, associated mineral grains, and small rounded ferruginous concretions are also present.

In the soil separates the coarse sand consists dominantly of sub-angular to rounded limestone fragments, with subordinate amounts of igneous rock fragments (including epidosite) and concretionary material. In the fine sand the suite of minerals is similar to that found in the 'kafkalla residue' except that opaline silica, though present, is scarce in all horizons of the profile. The clay fraction is composed mainly of mica and kaolin with subsidiary montmorillonite, palygorskite, and chlorite and trace amounts of quartz, goethite, and anatase. This suite is similar to that in the 'kafkalla residue' except for the presence of montmorillonite in the soil horizon with a concomitant decrease in the amount of palygorskite.

The appearance of the debris preparation and thin section of the A horizon is similar to that of the (B) horizon. Magnetite is more plentiful

and many grains are coated with dark brown iron oxide. Fine cracks are few but cavities are numerous and rounded aggregates with the Iwatoka phenomenon are evident. Neither fluidal structure nor oriented coatings on grains are present.

The soils described above have been distinguished by Reifenberg and Ewbank from 'terra rossa on limestone' described from the foothills of the Kyrenia Mountains. These high mountains are composed of dark grey Hilarion Limestone where, mainly on the south side, red-coloured friable soils are found. The surface is strewn with large limestone blocks and the sparse soil cover penetrates deep into fissures and cavities in the underlying rock. A sample of the A horizon was collected above Kythrea at 1,700 ft. O.D. When dry, the soil colour is red (2·5 YR 4/6) and the soil has a slightly hard, coarse to medium granular structure. Compaction increases with depth, but the surface is friable and easily worked when dry. The soil is somewhat stony and contains 52 per cent. clay, 25 per cent. silt, and is almost completely decalcified.

In thin section it can be seen that there are a few feldspathic rock fragments and the minerals include quartz, feldspar, magnetite (common), and a few amphiboles. Some calcite is present as infillings of former, roughly circular cavities, but there is none in the groundmass which is uniformly brownish-red and is not doubly refracting, nor are any fluidal structures visible. The fabric is spongy and there are numerous discrete rounded aggregates in which mineral grains are embedded. There are no shrinkage cracks, but owing to the shape of the aggregates, many cavities are present (Plate I *b*). Mica, chlorite, and kaolin are the dominant clay minerals; the 2:1 type minerals constituting approximately 70 per cent. of the fraction. Quartz, feldspar, and talc occur in trace amounts. The parent material, the situation, and properties of this soil lead to the conclusion that it is a mature terra rossa.

II. *Soils on Igneous Rock Material*

Reifenberg and Ewbank (1933) describe reddish and yellow-brown soils developed on diabase, with greasy red clay in the rock fissures, in situations which almost preclude any influence of calcareous sediments in their formation. South of Apliki at about 700 ft. O.D. a sample was collected at 12–14 in. of the (B) horizon developed on colluvium from igneous rocks. The soil is a yellowish-red (5 YR 4/6, dry) stony clay loam with 33 per cent. clay and when dry has a hard, coarse, subangular blocky structure. In a debris preparation it has a porphyropeptic fabric with a dense, waxy appearance. In thin section the fabric skeleton is seen to be composed of rounded to subangular fragments of igneous rocks and their associated minerals. The rock fragments are mainly of microdioritic type with relatively unaltered twinned plagioclase laths, though the original ferromagnesian constituents have been largely replaced by chloritic or serpentinous substances. Discrete mineral grains are mainly feldspar, magnetite, and epidote with quartz and amphiboles subordinate: in addition, there are a few small rounded ferruginous concretions. The groundmass is brown and dense with many fine sinuous cracks and irregularly rounded pores. Most of the groundmass

is unaggregated but there are a few large rounded aggregates. Between crossed polars fluidal structures become apparent, particularly around grains and rock fragments, and the groundmass appears to penetrate the latter. In the clay fraction X-ray examination showed the dominance of mica and montmorillonite in approximately equal amounts with accessory kaolin and trace amounts of goethite and feldspar.

This soil appears to be similar to that described by Reifenberg and Ewbank, and consideration of the factors involved in its formation and of its micromorphology leads to the conclusion that it should be classified as a rotlehm (Kubiena, 1948).

Red-coloured soils are very extensive in flat areas or on land with sharply rolling relief such as occurs north of the foothills of the Troodos Mountains. The soils occur on a conglomerate of rounded, igneous boulders, stones, and gravels which may or may not be cemented with calcium carbonate. The conglomerate has been deposited by flood-waters in roughly horizontal beds, and cementation, if present, is confined to the upper 3–4 ft., the remainder being loose and extending in places to over 100 ft. The soils are more or less stony with igneous pebbles and are usually about 3 ft. deep to the conglomerate. The boundary is clear but irregular, and the upper part of the cement is often stained red. A profile was examined 1 mile south of Kokkini Trimithia on level land at about 700 ft. O.D. and samples were taken of the (B) horizon at 18–20 in. and of the A horizon. When dry, the A and (B) horizons are dark red (2·5 YR 3/6) and red (2·5 YR 5/6), respectively, and the clay content increases from 42 per cent. in the A to 60 per cent. in the (B) horizon while the silt content is almost constant at about 14 per cent. There is approximately 5 per cent. of carbonate present usually in the form of secondary nodules and vertical veins of small crystals which are more obvious in the lower soil layers. Although the clay content is high, the soils are friable when dry and are easily worked. Compaction increases with depth, and the (B) horizon is hard when dry but plastic when moist. The structure passes from medium granular at the surface to cloddy or even massive in the subsoil.

In a debris preparation the (B) horizon has a dense porphyropeptic fabric with a waxy appearance and even the smallest aggregates are sharply angular. Examination of thin sections shows that calcite, filling former cavities, is present as rounded concretions of small crystals averaging about 5 μ in diameter, but no carbonate is disseminated in the groundmass. Rounded brown ferruginous concretions are sharply defined by smooth outlines from the groundmass and are brownish-red in reflected light. A few small fragments of igneous rocks, a moderate number of mineral grains, and a few nodules of secondary silica are also present.

A microscopic study of the separated sands enabled a more detailed examination to be made of their composition. The coarse sands (2–0·2 mm.) consist mainly of abundant angular to subangular igneous rock fragments; rounded and subangular, pinkish calcium-carbonate nodules, many being slightly porous and irregularly spherical, dark brown ferruginous concretions ranging up to 1 mm. in size. In the fine sands

(0·2–0·02 mm.) the minerals present are indicative of their origin from an igneous parent material, epidote, magnetite, amphiboles, and pyroxenes (greenish augite and hypersthene) making up the bulk of the heavy residues. Accessory minerals include zircon, apatite, garnet, tourmaline, and kyanite (very rare). Quartz and feldspars of varied composition are the dominant light minerals. Much of the feldspar (mainly orthoclase and albite) is highly altered and iron-stained, but accessory amounts of unaltered grains of sanidine, andesine, and bytownite are also present. Concretionary and chloritic material occur in minor amounts.

In thin section the groundmass is almost uniformly yellow-brown, but appears reddish-brown by reflected light. It is very dense, practically non-porous, and is split by fine sinuous cracks so that sharp-angled aggregates are formed (Plate I *c*). Between crossed polars fluidal structures become visible as numerous doubly refracting streaks, frequently following the cracks, and very evident as a coating around the large rock fragments and mineral grains (Plate I *d*). These anisotropic coatings and streaks show straight (though often shadowy) extinction and positive elongation which is consistent with their being composed of assemblages of clay flakes exhibiting a marked degree of parallelism and either oriented with their *c*-axes perpendicular to the surface of deposition as suggested by McCaleb (1954) or aligned in parallel due to plastic deformation as demonstrated by the laboratory experiments of Williamson (1955).

Mica, chlorite, vermiculite, and possibly montmorillonite in complex formation with much mica exsolved constitute approximately 80 per cent. of the clay fraction, the remainder being kaolin with feldspar and quartz in trace amounts.

The fabric of the A horizon is intermediate between porphyropectic and intertextic and has a dull, porous, granular appearance. The fabric skeleton consists of igneous rock fragments and associated minerals together with a few ferruginous concretions. Most of the groundmass, consisting of reddish-brown aggregates displaying the Iwatoka phenomenon, is dense with only a few pores and fine sinuous cracks and no fluidal structures are apparent. Some parts, however, are very dense, and have fluidal structures and the coating of grains with oriented clay as in the (B) horizon.

The profile therefore has an A horizon with a moderately well-developed earthiness and a (B) horizon having the properties of a rotlehm.

Discussion

The soil from the Kyrenia Mountains agrees with a frequently accepted definition of a terra rossa as a red-coloured, decalcified soil associated with hard limestone and has the morphological properties described by Kubiena (1954, p. 214). The dominance of the 2:1 type clay minerals in the A horizon suggests that it is the siallitic variety. This variety appears to be of widespread occurrence as Muñoz Taboadela (1953) has reported the dominance of illite in red soils (including terra rossa) of the Mediterranean region.

The examination of the profile north of Kokkini Trimithia shows that it has many of the properties of the terra rossa, but the presence of calcium carbonate which is being incorporated into the soil indicates that it is incompletely developed. The clay minerals in the soil correspond with those in the kafkalla residue and, in particular, palygorskite (attapulgite) is present in both. This mineral has been reported by Michaud *et al.* (1946) in terra rossas and other soil types derived from calcareous rocks in SE. France. In view of its occurrence in the kafkalla and overlying soil in Cyprus, it is probable that it is present in the soil as a residual mineral and not as a result of pedogenic processes; this probably applies to most of the occurrences of this mineral in soil horizons. Although igneous material is present in both the kafkalla and soil it plays only a minor part in the development of this profile.

The A horizon of the terra rossa has a characteristic micromorphology with discrete aggregates in which evidence of mobility of the constituents is entirely lacking. These features are apparent in the surface soil of the profile north of Kokkini Trimithia, but the aggregates are less apparent in the (B) horizon.

On the other hand, the (B) horizons of the soils associated with igneous material both at Apliki and south of Kokkini Trimithia differ in important respects from those considered above. Their micromorphology agrees with that of a rotlehm in that the groundmass is practically continuous (dense) and shows evidence of considerable mobility. One of the features of the profile south of Kokkini Trimithia is the presence of fragments with rotlehm characteristics in the otherwise 'earthy' surface horizon. Since it is unlikely that these have been brought to the surface by cultivation, they may be relics of the previous fabric of the horizon which now has the micromorphology of an erde. The profile appears to be analogous to that of the earthy braunlehm in which 'in regions with dry summers, a more or less strong earthiness can appear in the uppermost soil layers. . . . The underground layers usually retain a strong braunlehm character' (Kubiena, 1954, p. 223).

This short study of two soil types of wide extent in Cyprus has shown that they differ in important aspects and that micromorphological investigations enable them to be distinguished and assist in their classification.

Acknowledgements

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DESCRIPTION OF PLATE

I *a*. (B) horizon of terra rossa from Kokkini Trimithia, showing numerous cavities and cracks and, in the bottom left-hand corner, a limestone fragment penetrated by the groundmass. Ordinary light, × 100.

I *b*. A horizon of terra rossa from Kythrea with discrete, rounded aggregates and many cavities. Ordinary light, × 100.

I *c*. (B) horizon of rotlehm from Kokkini Trimithia, showing the continuous (dense) groundmass with fine cracks. Ordinary light, × 100.

I *d*. As I *c*, crossed polars, showing anisotropic streaks along cracks and as coatings around grains.

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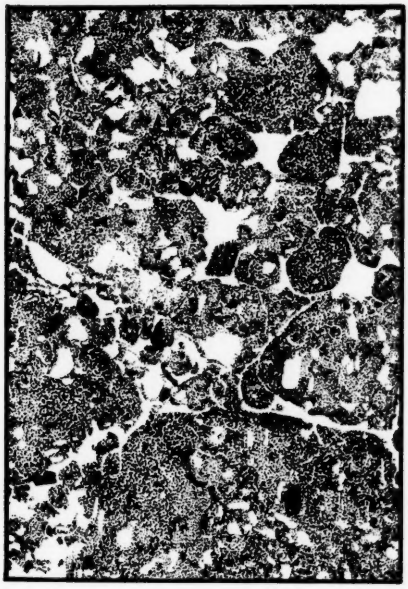
a



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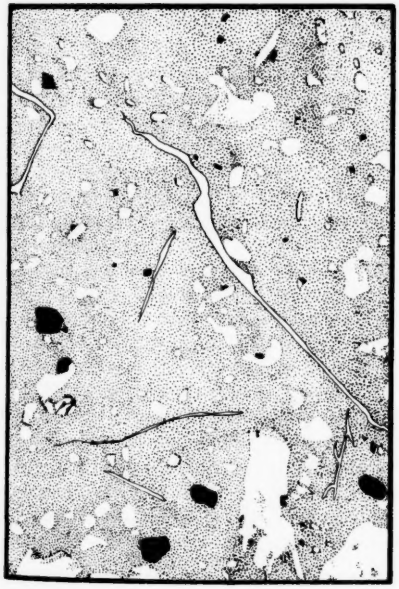

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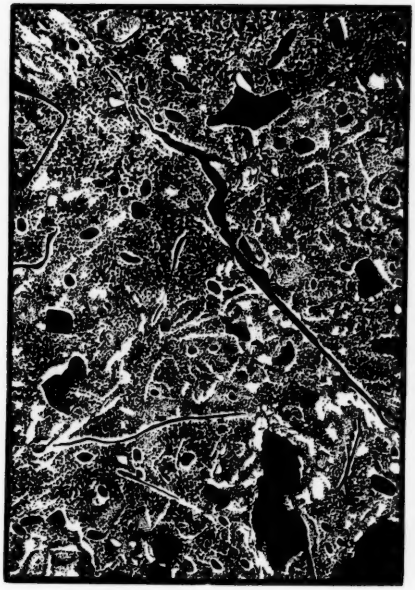

d

D. A. OSMOND AND I. STEPHEN—PLATE I

PERMEABILITY MEASUREMENTS IN THE FIELD AS AN ASSESSMENT OF ANISOTROPY AND STRUCTURE DEVELOPMENT

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Summary

Thirteen sites were examined and the permeabilities determined by a combination of the two-well (Childs) and the single-tube (Kirkham) methods. Anisotropy occurred in less than half of these sites. The range of permeabilities encountered was ten-thousand fold. Two of the clay soils have permeabilities comparable with those of gravelly sands.

An argument is presented for the use of permeability as an objective measure of structure in the field and the principal disadvantages of the permeability method are listed.

Variability in field structure is considered from the aspect of the ratio between the size of the well sample and the size of the structural units. Four cases of variability are interpreted in terms of their effect on the standard error and the asymmetry of results obtained by the two-well method. This interpretation is shown to allow of the assessment of field structure from the permeability results. When sub-units of structure and the experimental equipment have similar dimensions, individual determinations have questionable validity.

The method of calculating permeability and anisotropy from field data is given in an Appendix. A comparison of the field descriptions with the permeability results for the experimental sites indicates that qualitative profile differentiation does not always imply a change of permeability; neither can visual profile uniformity be taken to indicate uniform permeability.

Introduction

AN *in situ* method of measuring the hydraulic permeability of a soil below the water-table was described by Childs (1952) and Childs *et al.* (1953). This employed a pair of wells, between which steady-state flow was induced by establishing a constant-pressure head difference. It was shown that this method measures the horizontal components of hydraulic permeability. The results from such an experiment, combined with those from an experiment such as Kirkham's (1945) (which gives an 'apparent' permeability in the case of anisotropic soil), permit the calculation of the true vertical permeability. In the second paper (Childs *et al.* 1953), only measured values of horizontal permeability are listed. It is the purpose here to describe an investigation which measured both vertical and horizontal components of the permeability. This will be followed by a discussion of these results as affording a description of the degree of development of structure of soils below the water-table.

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Experimental

A typical installation is shown in Fig. 1. We describe, firstly, the two-well method, with modifications and details not included in Childs *et al.* (1953). Pairs of holes, 1 m. between centres, were excavated with a manually operated post-hole auger, 20 cm. in diameter. When digging, it is most convenient to take small 'bites' with the auger, for if

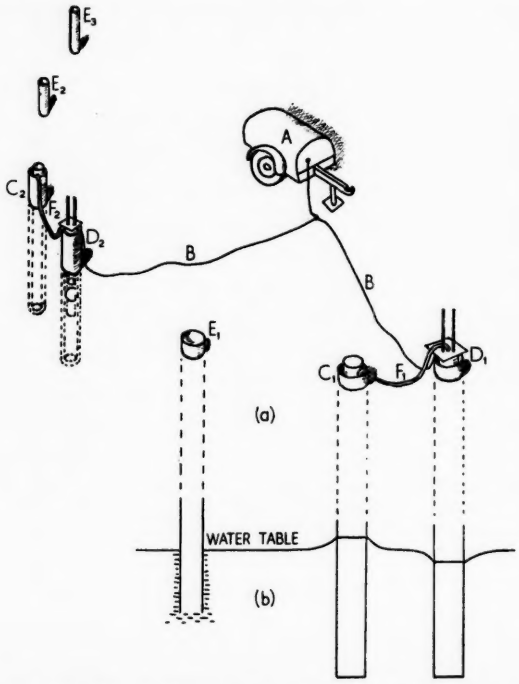

FIG. 1. Experimental layout at a site. A, Jeep trailer containing batteries; B, electric cables from batteries to pumps; C_1, sink well of pair 1; C_2, sink well of pair 2 at a different depth; D_1, pumped well of pair 1; D_2, pumped well of pair 2; E_1, E_2, E_3, open-ended Kirkham tubes sunk to different depths; F_1 and F_2, tubes conveying water from pumped wells to sink wells; G, pump; C_2 and D_2 are drawn to indicate subsurface arrangements. Diagram (*b*) illustrates in section the water-table from E_1 through C_1 to D_1.

one takes a deep bite, necessitating extraction of the auger by means of a tripod and winch one may puddle the sides of the hole. The well-holes were lined with a gravel pipe to support the sides against slumping. Each pipe consisted of two concentric cylinders, 8 and 17 cm. diameter, 150 cm. long, of 8×20-guage steel mesh, closed at one end with mesh; the annular space was filled with gravel of average size $\frac{1}{2}$ cm. This pipe was lowered down the axis of the hole and the small outer space between

the pipe and the sides of the hole filled with gravel. On leaving a site, only this latter small quantity of gravel had to be abandoned, the gravel in the pipe remained clean enough for several sites. In some clay soils encountered, it was not necessary to fill this outer space with gravel since there was little tendency for the hole to collapse.

The maximum depth to which measurements were made was about 180 cm.; this was determined solely by the arbitrary length of the wells. In soils where obvious profile differentiation occurred, the wells were dug to reach the base of the first horizon below the water-table and were deepened in subsequent experiments. The top of one of the gravel pipes served as a platform to support the pump. This was a small centrifugal impeller pump (ex-government aircraft petrol pump) worked from a 24 volt D.C. supply. (To keep the batteries charged, a petrol-driven generator was part of the field equipment.) The pump fitted down the centre of the gravel pipe, and the setting of its depth from the top of the pipe determined the depth of lowering of the water level in this well. The water from the pumped well was delivered to the second well. When equilibrium was reached, i.e. when the water levels in both wells were steady, the rate of flow was determined by measuring-cylinder and stop-watch, whilst water from another cylinder was simultaneously poured at an equivalent rate into the sink well to prevent disturbance of the equilibrium. The flow was then reversed by transferring the pump to the other well. Duplicate values of permeability obtained by reversing the flow between wells always agreed well, if equilibrium was attained.

If the level in the pumped well, $W1$, was lowered by (say) 5 cm., it was rarely that the level in the sink well, $W2$, would rise by exactly 5 cm. as it should if the site was symmetrical about a plane in which the wells were images of each other. Some idea of the degree of variability of the soil site can perhaps be obtained from this behaviour of the wells, which we propose to call 'asymmetrical' behaviour. For example, if the water level in well $W1$ is lowered by 5 cm., and the level in well $W2$ rises by 2 cm. we know that the soil in the vicinity of well $W2$ is more permeable than near well $W1$, though a quantitative analysis of this phenomenon has not yet been attempted. On reversing the flow, lowering the level in well $W2$ by 5 cm. would cause a rise in well $W1$ of $5 \times 5/2 = 12{\cdot}5$ cm.; and the rate of flow would be $2{\cdot}5$ times as great in this reversed direction, $W2$ into $W1$, than in the original 1 into 2. An example of the calculation of permeability from observed quantities in a two-well experiment is given in Appendix I.

The second experimental method used in this investigation consisted primarily of the measurement of the rate of rise of the water level in a lined well through which water can only enter through the floor. For convenience we shall call this a Kirkham-tube experiment (see Kirkham, 1945). The single hole for the Kirkham-tube experiment was dug with the same post-hole auger, and lined with a steel tube, which was driven in in stages by a 27-lb. hammer (sliding on a guide integral with an anvil, temporarily fitted to the tube head) and the soil extracted by the auger. In the final stages, soil was removed by a specially designed auger, known as a 'canister'; basically this was a shallow, cylindrical bucket, braced

and mounted on a long rigid handle, just able to fit inside the tube. When the 'canister' was turned, a knife-edged slot in the bottom of the bucket cut and admitted a thin slice of pared soil into the auger, and in the final operation prepared a flat, horizontal surface to the soil level with the bottom of the liner, which in the terminology of Kirkham became a cavity of zero length. The steel-tube liner was slightly larger than the diameter of the hole bored with the auger; in this way the driven tube was sealed to the soil, and there was little likelihood of the formation of a leak path between the soil and the liner. However, this made the liner hard to insert in some soils, and in such cases the hole, down to the water table, was enlarged using the canister wall as a scraper. The maximum depth to which measurements with the Kirkham tubes were made by reason of their length was 180 cm. For convenience in interpretation of the data from this method in conjunction with that from the two-well method, the end of the Kirkham tube was located as far as was possible at the mean depth of the interval spanned by the two-well method. After use the liner was pulled out with a winch and tripod. An example of the calculation of permeability from observed values of a Kirkham tube experiment is also given in the Appendix.

Our experience confirms that of Kirkham, that it is preferable to pump out the tube and allow water to flow into the cavity from the soil, rather than to allow emptying of an artificially water-filled cylinder into the soil. The first procedure keeps open the conducting channels in the soil at the surface of the cavity.

Résumé of the Theory

For an anisotropic soil, the equation of continuity is,

$$K_x\frac{\partial^2\phi}{\partial x^2}+K_y\frac{\partial^2\phi}{\partial y^2}+K_z\frac{\partial^2\phi}{\partial z^2}=0, \tag{1}$$

where K_x, K_y, and K_z are the components of permeability in the direction of the coordinate axes x, y, and z, and ϕ is the potential of the soil water, expressed in ergs per c.c. We shall take z to be the vertical direction.

A change in scale, viz:

$$\lambda=(K_x/K_y)^{\frac{1}{2}}y=\alpha y, \tag{2}$$

and

$$\mu=(K_x/K_z)^{\frac{1}{2}}z=\beta z, \tag{3}$$

transforms equation (1) to Laplace's equation,

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial\lambda^2}+\frac{\partial^2\phi}{\partial\mu^2}=0. \tag{4}$$

The analysis of the two-well experiment and of the Kirkham-type experiment may then proceed in the isotropic transformed space, in which the permeability is

$$K'=K_x/\alpha\beta=(K_y.K_z)^{\frac{1}{2}}. \tag{5}$$

Two-well method

However, the treatment of the two-well system is simplified by two devices which return it to a problem in an isotropic, horizontal plane. Firstly, for these experiments, it is assumed that the soils are isotropically permeable in the horizontal plane, i.e. α, of equations (2) and (5), has the value unity. Secondly, it has been shown that the flow between the wells which occurs below their ends, and which hence involves the vertical component of permeability, may be described quantitatively by an end-correction (l_f) added to the measured length of the wells (Childs *et al.*, 1953). It is the length of well which would be required to accommodate the additional truly horizontal flow at a rate equal to that of the end flow. Then, the horizontal permeability, from the results of the two-well experiment, is given by

$$(K_x = K_y) = K_h = \frac{\chi \, dQ/dt}{(l+l_f).\Delta\phi} \tag{6}$$

in which dQ/dt is the rate of flow between the wells in c.c. per sec. and l is the distance of penetration of the wells below the water-table; l_f is the appropriate end-correction; $\Delta\phi$ is the difference in potential between the wells causing the flow; and χ is a geometrical factor involving the dimensions of the installation, and is given by

$$\chi = \frac{1}{\pi}\left(\cosh^{-1}\frac{d}{2r}\right) \tag{7}$$

where r is the radius of each well, and d is the distance between centres: for our system $r = 10$ cm., $d = 100$ cm. and χ has a value of 0·735. $l_f = 20$ cm. in an isotropic soil and $20/\beta$ in anisotropic cases.

Kirkham-tube method

Analysis of the Kirkham tube experiment must proceed in the isotropic transformed space, although we continue to assume that soil is isotropic in the horizontal plane. The permeability, K', is given by

$$K' = \frac{\pi r^2}{g\rho A} \frac{\log_e z_1/z_2}{t_2 - t_1}. \tag{8}$$

In this expression, r is the radius of the cavity (of zero length), g the gravitational acceleration, ρ the density of water, and t_1 and t_2 are the times at which the distances of the water level from the equilibrium level are z_1 and z_2 respectively. A is a factor dependent on the geometry of the system, but which cannot be calculated by substitution of dimensions in a simple formula as can χ. Luthin and Kirkham (1949) measured A by an electrical analogue model and gave conditions for which their values may be applied with reasonable accuracy; for the experimental situation described A has a value of 51 cm.

A cavity of zero length shows the greatest degree of discrepancy between apparent permeability K' and true horizontal permeability K_h for soils with anisotropic permeability. Furthermore, a cavity of zero length in anisotropic soil is still one of zero length in the isotropic transformed space, so that the A value given by Luthin and Kirkham may be used

in equation (8) even though the degree of anisotropy has yet to be found.

When K_h and K' have been determined by the two-well and Kirkham-type experiments respectively, the permeability of the soil can be completely specified, since K_v $(= K_z)$, is given by,

$$K_v = \frac{K'^2}{K_h} = \frac{K_h}{\beta^2}. \tag{9}$$

Experimental Results

Measurements on six soils in Romney Marsh, and five soils in Bedfordshire, were made during the summer of 1955. These results, together with a brief description of each soil, are given in Table 1. Two soils

TABLE 1

Location of site and soil texture	K_h *c.g.s. units** @ 20·2° C.	*Interval of measurement*	*Anisotropy* K_h/K_v	*Asymmetry*
Romney Marsh Soils: Hastings Sheet, O.S. 1 in. map, No. 184				
Site 1 016248†	$5{\cdot}8\times10^{-7}$ ±0·8 (3)	33–117 cm.	1 (4)	1·5
	$1{\cdot}7\times10^{-6}$	117–52 cm.	..	
Site 2 015247	$1{\cdot}6\times10^{-6}$ ±0·1 (2)	125–170 cm	1 (2)	1·2
Site 3 978249	$8{\cdot}0\times10^{-7}$ ±0·7 (4)	40–162 cm.	1 (5)	1·7
Site 4 054277	$1{\cdot}1\times10^{-7}$ ±0·1 (4)	61–169 cm.	0·028 (3)	1·25
Site 5 060201	$3{\cdot}6\times10^{-5}$ ±0·7 (4)	74–160 cm.	50(2) @ 110 100 (2) @ 140	3·0
Site 6 063323	$2{\cdot}0\times10^{-5}$ ±0·5 (4)	42–124 cm.	1 (2) @ 71 200 @ 94 70,000 @ 113	4·3
Bedforshire Soils: Bedford and Luton Sheet, O.S. 1 in. map, No. 147				
Site 1 023329	$3{\cdot}9\times10^{-6}$ ±0·4 (4)	40–156 cm.	40,000 (2) @ 100 200 (2) @ 110	1·4
Site 2 024330	$3{\cdot}6\times10^{-7}$ ±1·0 (3)	60–175 cm.	1 (3)	2·0
Site 3 077375	$4{\cdot}3\times10^{-7}$ ±0·4 (4)	40–160 cm.	1 (2) @ 100 0·006 (2) @ 128 & 155	1·4
Site 4 113389	$1{\cdot}2\times10^{-6}$ ±0·1 (4)	20–157 cm.	1 (4)	1·2
Site 5 169560‡	7×10^{-8} ±2 (2)	70–175 cm.	1	1·1
Cambridgeshire Soils: Cambridge and Ely Sheet, O.S. 1 in. map, No. 135				
Site 1 425605	$1{\cdot}4\times10^{-5}$ ±0·1 (3)	80–120 cm.	1 (3)	1·1
Site 2 421599	[$3{\cdot}6\times10^{-9}$ ±0·1 (3)	60–158 cm.	Kirkham-Tube results only.]	

* $6{\cdot}9\times10^{-7}$ c.g.s. equal to 1 in. per hr.

† Coordinates of site on Ordnance Survey Sheets.

‡ Huntingdon and Peterborough Sheet, O.S. 1 in. map, No. 134.

on the University Farm, Cambridge, which were examined in the spring of 1956, are also included. The smallest number in the interval column represents the water-table depth below the soil surface. The bracketed figure after a result refers to the number of sampling positions (taking a change of either depth or location as a change of position) to derive the Standard Error of the means. The degree of anisotropy, K_h/K_v, refers to particular depths in the profile. The degree of asymmetry, listed in the last column, is the mean of the values derived from the total number of observations in the two-well experiment; in counting the total number of observations a reversal of flow counts as a separate observation.

Discussion

(*a*) *Anisotropy*

In this discussion, anisotropy will be confined to the numerical ratio of the horizontal permeability, K_h, to the vertical permeability, K_v, measured over the same interval in the profile. The horizontal permeability, as has already been noted, has been derived assuming that in all directions in a horizontal plane the permeability is constant. An isotropic soil is one of which the horizontal and vertical permeabilities at a point are equal. An isotropic soil is not necessarily a homogeneous one since the values of permeability may vary with position. An anisotropic soil has the ratio K_h/K_v either greater or less than unity, depending on whether the ease of horizontal movement of water is greater or less than the ease of vertical movement.

Approximately half of the soils investigated proved to be anisotropic. The Romney Marsh soils were all alluvial mineral soils; those that proved to be anisotropic had a more highly developed structure by visual observation, although anisotropy was not observed visually, except at site 5. The soils at sites 1, 2, and 3 were isotropic, the permeability increased as the texture became sandier. At sites 5 and 6 the horizontal component of permeability, K_h, was much larger than the vertical component, K_v. At site 5, at a depth of about 100 cm., the soil became laminated with alternating bands of clay and fine sand, each about 5 mm. thick, and which appeared to be bedded horizontally. This gives rise to the anisotropy found at depths below 110 cm. In addition, the soils at both sites 5 and 6 were much fissured below the water table, and the permeability values in these soils were very much higher than a consideration of texture would lead one to expect. It is perhaps surprising that large cracks should exist below the water table. While the wellholes were being dug relatively clear water rapidly flowed into the holes from these cracks. Swelling of the clay would eventually close any shrinkage fissures produced by a temporary drying of the clay. In these two soils the water table has been present for many years, certainly time enough for a normal clay to close cracks caused by drying alone. However puzzling the phenomenon may be, it is certain that the present fissures are a permanent feature of these soils and account for their high permeability.

The soil at site 4 had a somewhat greater permeability in the vertical than in the horizontal direction. Fissures occurred in this soil but not

to the same extent as in the two soils just described, and the permeability is correspondingly much smaller.

In Bedfordshire the soils were alluvial peats or peaty loams, with the exception of the soil at site 5, which was an alluvial clay. Sites 1 to 4 all lie on the northern bank of a minor tributary of the Great Ouse; with site 1 farthest upstream. Site 5 was in the valley of a major tributary. Anisotropy was exhibited by two of these five soils; at site 1 K_h was greater than K_v, and at site 3 K_h was less than K_v. Peat soils often have a laminated appearance, particularly in the fibrous organic horizons, and anisotropy would therefore be expected as a normal characteristic; previous work (unpublished) has supported this belief, but only two out of four soils were conformal in this area. Sites 1 and 2 were 100 yds. apart in the same field, and superficially appeared by no means as distinct as the permeability results show them to be; site 1, for all practical purposes, has K_v equal to zero, whilst site 2 is isotropic; the absolute values of K_h are also markedly different at the two sites.

In Cambridgeshire the two soils examined were almost diametrically opposite in their properties. One soil, being a glacial gravel soil with a permeability almost as great as the highest recorded, is isotropic as would be expected of a cohesionless gravelly system. At site 2, situated on an exposure of the gault clay of the cretaceous system, the permeability was so small that it was impracticable to use the two-well method and results were obtained from the Kirkham tube method alone. It is necessary to know the position of the water table at equilibrium for calculation of permeability values by this method. This could not be directly observed in this material and the position of the water table and the permeability were observed by observing the rate of rise in two tubes simultaneously under different heads, and by solution of two simultaneous equations each with two unknowns (permeability and height of the water table). These observations were made continuously throughout the spring of 1956 both before and after rainstorms sufficient to saturate the soil to the surface. Intervals of 24 hrs. were required to measure changes in the water level of the order of 1 cm. in the Kirkham tubes. The water table was found to fall rather quickly after a rainstorm had brought it to the surface (to 60 cm. in 4 days) but thereafter fell much slower, until the tubes successively failed to penetrate it. (In this connexion it is perhaps of significance that this site had been mole-drained to 56 cm. in 1952.) From all these numerous observations over many weeks, the permeability remained constant for three tubes at depths greater than 60 cm. The gault clay subsoil has a 'massive' structure and the smallest yet recorded permeability of an undisturbed subsoil, being a ten-thousandth of the highest recorded permeability (also a clay, Romney 5).

(*b*) *Permeability and structure*

The magnitude of the hydraulic permeability of soils has most often been correlated with texture, since, in the absence of cracks and fissures, the pore size distribution which dominates permeability is related to the particle size of the material; the smaller the particles, the smaller

the pores and the very much smaller is the permeability. (For a discussion of this topic see Childs and Collis-George, 1950.) However, comparison of sites 4 Romney and 5 Bedford with site 6 Romney, which texturally were very similar, illustrates the inadequacy of this concept and the dominant effect of structure upon permeability.

The concept of soil structure may prove ultimately to be incapable of definition in such precise terms as to permit of quantitative assessment, but important physical properties of soil, such as permeability, which are dominated by structure are not thus restricted. It may be accepted that a measurement of permeability is directly applicable to field-water control measures, and thus designers of drainage systems who assess soil solely in textural terms may be seriously misled. Further, the soil surveyor, who customarily takes cognizance of the water régime in soil, may find a measure of permeability to be a more reliable guide to this end than is a textural assessment and in addition a diagnostic aid in the differentiation between soils of different structures. It is fair to say that the method suffers from three disadvantages. Firstly, although the method is inherently simple the equipment is comparatively expensive, £125 as at 1 January 1956. Secondly, the time and labour is not inconsiderable. Under ideal conditions, it takes two men an afternoon to install two pairs of wells and four Kirkham-type tubes. After the water table has reached equilibrium overnight, the observations can be completed the following morning and permeabilities calculated preparatory to commencing the next site the same afternoon. If the results show need for further information, e.g. pronounced profile differentiation or very great site variability, 24 hours are required for each further set of results. Site 2, Romney, was completed in 24 hours, whereas site 1, Bedford, took 3 days to complete. A third disadvantage is that permeability measurements can be made only in that part of the profile below the water table; consequently the site may have to be studied in the winter in order to obtain determinations as near to the surface as possible, and it is only in exceptional sites, such as river meadows, that the experiments can be carried out in summer.

Variability in the permeability of a site

We may now turn to a consideration of the variability of the soil permeability over the site and the significance to be attached to its value.

The flow of water is never uniformly distributed over the cross-section of a flow column, but is concentrated in the pore space and avoids the solids. When, however, the cross-section is large compared with the distance between pores the 'fine structure' of the flow is not perceptible and the concept of uniformly distributed flow implicit in a statement of Darcy's law follows. We may call a column of this kind a sufficiently large sample. This uniformity of distribution has been assumed in deriving the theory of flow of soil water to cells and cavities, but we need to examine the consequences of non-fulfilment of the conditions necessary for its validity, in the light of our experimental results.

We may distinguish a number of cases according to the ratio between the size of a well and the mean distance of the conducting channels:

(*a*) The well dimensions are large compared with the scale of the soil structure, i.e. the sample is sufficiently large, and the structure is uniform over the site.

(*b*) The sample is sufficiently large but the structure is not uniform; it varies with horizontal distances which are large compared with the size of the sample, or with depth, or both together.

(*c*) The sample (well) dimensions are of the same order as the scale of soil structure, i.e. the sample is insufficiently large, but the structure is uniform over the site.

(*d*) The sample is insufficiently large since the scale of structure is large, and the structure varies with distances which are large compared with the size of the sample.

The relation of (*d*) to (*c*) is as (*b*) to (*a*).

We may take cases (*a*) and (*b*) together, for it is safe to say that the simple situation of case (*a*) is unlikely and even if it were investigated its perfection would be masked by the imperfection of the method—it is approached by sites 2 Romney and 1 Cambs.—and that large samples are almost invariably examples of case (*b*) with greater or lesser degree of variability of permeability with depth or location. The degree of variability will be reflected in the standard error associated with the site, and this error will include also experimental errors associated with the equipment and with modification of the soil which may be caused by the process of installation. Much qualitative evidence of the degree of variability to be expected will come to light during the soil borings which are made as a preliminary reconnaissance of the site as well as during the subsequent installation of the wells, and such reconnaissance, by assisting one to restrict comparison to a particular soil series or to a particular horizon, can do much to reduce the standard error. It is rather surprising that only one site was encountered (site 1, Romney) in which horizons of different permeability were recognized and subsequently confirmed.

The purpose of the permeability measurements will decide whether a given degree of variability is acceptable or not. If it is excessive, a more detailed experimental survey of the site is indicated.

Cases (*c*) and (*d*) are readily distinguishable from (*a*) and (*b*), for if the sample defined by the well size is insufficiently large there is a high probability that each individual well of a pair is sited in a zone of different permeability; the basis upon which analysis rests is inapplicable, and indeed it is doubtful whether the very concept of soil permeability is valid in the circumstances. The practical consequence is that the wells are asymmetrical, the levels of water being perturbed by different amounts above or below the unperturbed water table. Such appreciable asymmetry is indicated in sites Romney 5 and 6, confirming the conclusion on other evidence that the permeability here is a structural phenomenon. In these circumstances the only impeccable course is to admit that the analysis is inapplicable and that a larger sample, using larger wells, must be resorted to, and this may be impracticable. To make

some progress when the asymmetry is not too great, one may apply the method in faith and, in effect, enlarge the sample without enlarging the wells by repeating the measurement at several locations. Since a change of well location by a few decimetres may be as effective in changing the structure sample as a change of many metres, one would expect the variability, as well as the asymmetry to be large, and this is shown to be so in sites 5 and 6 Romney. In case (*d*) a real change of structure with location may be revealed, if sufficiently large, in spite of the masking effect of inadequacy of sample size.

One may summarize by saying that while the results of a two-well experiment are not, in cases (*c*) and (*d*), capable of unambiguous interpretation, nevertheless the evidence of all kinds (permeability in relation to texture, asymmetry, and variability) taken together enables one to reach a sufficiently reliable conclusion for most practical purposes, and no doubt greater experience will improve the reliability.

A discussion of three examples taken from Table 1 will illustrate the concepts of variability outlined above.

Site 4, Bedford. K_h has a very small random error, the soil is isotropic, and the degree of asymmetry only 1·2 (unity represents symmetry). These results imply that the individual locations and depths investigated have very similar structures and that the variation within the soil composing each sample is small, i.e. this site approximates to case (*a*).

Site 5, Bedford. K_h has a large standard error, the soil is isotropic, and the degree of asymmetry small. Thus the areas sampled are large enough, but there is a change of soil structure over the site on moving from one location to the next; an example of case (*b*).

Site 6, Romney. K_h has a large standard error; the soil is anisotropic, the degree of anisotropy varying with depth; the degree of asymmetry is large. Thus the samples are too small to give a representative value of K_h and additionally the site has very marked structural variation vertically. For lack of further evidence it can be presumed that the site is uniform on moving from one location to another, but that the flow planes bounding the structural units are repetitive at a distance of the order of the dimensions of a well, viz. of the order of 20 cm.

In conclusion, therefore, it would be expected that highly structured soils would be most likely to have large sampling errors, since firstly the sampling size of the two-well experiment becomes relatively smaller compared with the size of the structural units and secondly the insertion of the wells themselves is likely to cause greater disturbance, and this disturbance being fortuitous may increase the asymmetry of the site relative to that of the site proper. The experimental evidence does not support this disturbance hypothesis, since in soils of low structural development it is noted that the asymmetry is generally small, even in soils which texturally would lend themselves to puddling. This would suggest that the method of installation of the wells does not disturb or smear the area around the wells which would be detected by an increase of asymmetry. Consequently in those soils where asymmetry is high, this asymmetry can be atrributed solely to the structural development inherent in that soil.

Acknowledgement

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APPENDIX I

Calculation of Permeabilities from Field Results for Site 5, Romney

1. *First approximate calculation of* K_h

Rate of flow, dQ/dt, between wells, 500 c.c. in 15 sec. at 12·5° C.
Water level lowered in pumped well by 10·0 cm.
Water level raised in second well, 4·3 cm.

(Asymmetry of wells: $10/4{\cdot}3 = 2{\cdot}4$.)

Potential difference, $\Delta\phi$, between wells, 14·3 ρg ergs per c.c.
Penetration, l, of wells below water table, 38·0 cm.
End correction, l_f (1st approx. with $\beta = 1$), 20·0 cm.
$l+l_f$, 58·0 cm.
χ (see résumé of theory), 0·735.

$$K_h = \frac{\chi . dQ/dt}{(l+l_f).\Delta\phi} = 3{\cdot}0 \times 10^{-5} \text{ c.g.s.}$$

2. *First approximate calculation of* K_v

When using equation (8) to calculate K', it is convenient to plot firstly $\log_e z$ against time, and obtain the mean value of $(\log_e z_1/z_2)/(t_2-t_1)$ from the slope of the resultant line.

Tube sunk to 110 cm. below the surface.

$(\log_e z_1/z_2)/(t_2-t_1)$, 2·85/3,000 sec.$^{-1}$.

A-function, 51 cm.

$\pi r^2/g\rho A$, $6{\cdot}20\times10^{-3}$ c.g.s.

$$K' = \frac{\pi r^2}{g\rho A}\log z_1/z_2\frac{1}{(t_2-t_1)} = 6{\cdot}0\times10^{-6} \text{ c.g.s. at } 12{\cdot}5^\circ \text{ C.}$$

$K_v = (K')^2/K_h$ (equation 9) $= 1{\cdot}20\times10^{-6}$ c.g.s.

3. *Successive approximation of* K_h *and* K_v

From the first approximations, we see that the soil is anisotropic. From equation (9) $K_v = K_h/\beta^2$, β (2nd approx.) $= 5$.

End correction, l_f (equals $20/\beta$) $= 4$ cm.

The second approximate value of K_h can now be calculated as in section 1 $= 4{\cdot}15\times10^{-5}$ c.g.s., and second approximate value of $K_v = 0{\cdot}865\times10^{-6}$ c.g.s.

Successive approximations are repeated until β, K_h, and K_v are constant. (In this example, one stage further is required.)

$K_h = 4{\cdot}25\times10^{-5}$; $K_v = 8{\cdot}5\times10^{-7}$ c.g.s. at 12·5° C.; $\beta = 7$.

Anisotropy at 110 cm. depth, $K_h/K_v = 50$.

Asymmetry = 2·4.

In practice, a number of replicate measurements of K_h and K' are made at each site, and a convenient calculation procedure is to calculate firstly the mean values of K_h and K', and then from statistical considerations decide whether they differ significantly, before calculating individual results, as outlined above.

APPENDIX II

Description of Soils at Experimental Sites of Table 1

A. *A Description of Romney Marsh Soils* by R. D. Green and G. P. Askew, of the Soil Survey of England and Wales and Wye College, Kent, respectively.

Site 1

0–30 cm.	Grey-brown clay loam, mottling becoming noticeable at about 20 cm.
30–55 cm.	Grey and brown mottled sandy clay.
55–180 cm.	As above, but texture gradually becoming lighter.
180–90 cm.	Blue silt.
190–260 cm.	Black peat, becoming browner with increasing depth.

Site 2

0–10 cm.	Brown loam to sandy loam.
10–180 cm.	Gradual change of texture from light brown sandy loam at 10 cm. to fine sand at 180 cm.
180–370 cm.	Fine sand.

Site 3

0–20 cm.	Brown loam to sandy loam.
20–150 cm.	Brown mottled fine sandy loam with texture becoming increasingly heavy with depth.
150 cm.	Peat appears and continues to depth of augering.

Site 4

0–10 cm.	Friable loam to clay loam, high organic content.
10–20 cm.	Grey-brown clay loam.
20–180 cm.	Grey-brown clay loam to clay, texture becoming increasingly heavy with depth. Mottling first appears at 30 cm.

Site 5

0–35 cm.	Brown and grey-brown clay loam.
35–55 cm.	Light brown and grey mottled clay loam.
55–100 cm.	Light brown and grey mottled clay with sand pockets appearing, the texture becoming increasingly sandy with depth.
100–240 cm.	Brown and grey mottled fine sandy and silty loam, texture becoming lighter with depth.
240 cm.	Sandy silt.

Site 6

0–20 cm.	Dark brown clay loam.
20–40 cm.	Light brown clay loam to clay.
40–140 cm.	Light brown mottled clay becoming blue-grey and shelly with depth. Structural fissuring well developed.

B. *A Description of Bedfordshire Soils*

Site 1

0–20 cm.	Dark brown peaty, silty loam.
20–120 cm.	Brown and red peaty silt, still structured organic residues.
@120 cm.	Gravel layer.

Site 2

0–22 cm.	Red sandy clay loam.
22–45 cm.	Red sandy loam.
45–105 cm.	Grey-brown light silt.
105– cm.	Greensand and gravel.

Site 3

0–18 cm.	Dark brown sandy loam.
@18 cm.	Large iron concretions.
18–36 cm.	Brown sand.
36–51 cm.	Mottled gravelly sand.
51–78 cm.	Black silty peat.
78–165 cm.	Dark brown fibrous peat.

Site 4

0–10 cm.	Black peaty sand.
10–40 cm.	Black silty sandy peat.
40–80 cm.	Dark brown fibrous peat.
80–150 cm.	Silty sand with gravel.

Site 5

0–20 cm.	Dark brown clay loam.
20–80 cm.	Brown and grey clay.
80–100 cm.	Grey clay.

C. *A Description of the Cambridgeshire Soils*

Site 1

0–15 cm.	Dark brown, loamy sand, gravelly.
15–60 cm.	Light brown sandy gravel.
60–120 cm.	Yellow sand with gravel pockets.

Site 2

0–10 cm. Dark brown clay loam, high organic matter content and large earthworm population, calcareous.
10–30 cm. Buff clay, calcareous.
30–60 cm. Mottled, pale grey-brown and orange-brown clay, highly calcareous.
60–180 cm. Blue-grey clay, sticky and plastic, highly calcareous.

THE ANISOTROPIC HYDRAULIC CONDUCTIVITY OF SOIL

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Summary

When discussing soils with anisotropic hydraulic conductivity it is usual to assume for simplicity that the three directions in which the principal conductivities may be specified are mutually perpendicular, i.e. they may be taken as the axes of a system of rectangular cartesian coordinates. It is usually readily agreed that this assumption is plausible since the structural fissuring to which anisotropy is due is, in nature, predominantly horizontal and vertical. It is shown here that the assumed property is in no way dependent upon such restrictions of direction of the contributory fissures, but that provided the conductivities of the individual contributors themselves are characterized by mutually perpendicular axes, then any combination of the contributors in any directions results in a total conductivity which also has three mutually perpendicular axes.

It has long been recognized that soils may have the property of anisotropic hydraulic conductivity, that is to say they may conduct water more readily in certain directions than in others. The absence until recently of a ready means of measuring anisotropic conductivity in the field has resulted in a situation where on the one hand speculation has tended to lay great emphasis on the frequency and magnitude of anisotropy and yet, on the other hand, quantitative practical matters such as the design of drainage systems have inevitably proceeded without any reference to such a property. The development of a practicable field technique for measuring hydraulic conductivity without any assumptions about the presence or absence of anisotropy (Childs, 1952; Childs *et al.*, 1953) has, by taking the subject out of the realm of speculation, had two consequences. Firstly it has made it worth while to solve the drainage problem for anisotropic soils (Edwards, 1956) and secondly it has been possible to show, in so far as brief experience can yet show, that the frequency of occurrence of appreciably anisotropic conductivity may have been overestimated in past speculations (Childs, Collis-George, and Holmes, 1957).

In discussing anisotropic conductivity it has been usual to take it for granted that there are three mutually perpendicular principal axes, such that a potential gradient in the direction of a principal axis produces a flow of water in that direction and in no other. Values of hydraulic conductivity may thus be specified for those directions, and if the values are different in each of the three directions, or in any two of them, the material is said to be anisotropic. It follows that a potential gradient in any direction other than that of a principal axis produces a flow of water in a direction other than that of the potential gradient. It should be emphasized here that because anisotropic conductivity of soil is recognized to be associated with structural fissuring, and because such fissuring is predominantly vertical and horizontal, it is usually readily

conceded that the directions of the principal axes should include the vertical and horizontal directions, i.e. two directions mutually at right angles, and there is no evidence and no reason to expect that soils should be anisotropic in respect of different horizontal directions. Nevertheless there is no self-evident reason why the principal axes should in general be mutually perpendicular and in private communications it has been held to be a defect of analysis that such a condition should be assumed. The purpose of this paper is to show the assumption is valid far more generally than has been supposed hitherto. It would be very desirable to show on the most general grounds of the Stokes–Navier equations of viscous fluid flow that the principal axes must be mutually perpendicular, but this has not yet been possible.* What is shown here is that the condition is obeyed by very general systems of fissures, and not only by systems of vertical and horizontal fissures.

It may be supposed that the very fact of anisotropy implies that flow is restricted to certain preferred paths irrespective of the direction of the potential gradient which causes the flow. Thus, to choose an over-simplified model for purposes of illustration, a single tube can conduct water only in the direction of its axis, no matter what may be the direction of the force acting. The impelling force may be resolved into components in and perpendicular to the direction of the axis, and only the former is effective. Again, a plane structural fissure can conduct water in any direction which lies in the plane, but in no other. In practice structural fissures meander but may be regarded as meandering about a mean direction. The meandering constitutes a micro feature superimposed on the extensive mean pattern of flow which is the subject-matter of Darcy's law. The kind of problem in which Darcy's law is invoked is commonly one in which the flow path from source to sink has a length measured in tens of metres, so that meandering to the extent of tens of millimetres or even centimetres is not noticeable on this scale. We shall therefore take as our models (*a*) systems of plane fissures, such that water movement in a particular fissure is restricted to the plane of that fissure but may be in any direction equally in that plane according to the direction of the impelling force, and (*b*) systems of doubly restricting fissures in which water movement is confined to a particular characteristic direction.

Darcy's Law for Anisotropic Conductivity

As is usual in discussing hydraulic conductivity we express the rate of water movement in terms of the effective velocity $\mathbf{v}$, which is the volume of water per second which crosses a unit area of soil perpendicular to the direction of flow. For isotropic soils Darcy's law takes the well-known form

$$\mathbf{v} = -K \operatorname{grad} \phi, \qquad (1)$$

where ϕ is the hydraulic potential function. Since $\mathbf{v}$ and grad ϕ are in the same direction, the conductivity K may be regarded simply as a

* The author is indebted to Mr. J. R. Philip of the C.S.I.R.O., Deniliquin, N.S.W., Australia, whose researches into the general consequences of the Stokes–Navier equations operating in porous media led to the present more restricted study.

scalar quantity. If the material has anisotropic conductivity then only exceptionally is $\mathbf{v}$ in the same direction as grad ϕ. Let $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ be unit vectors in the respective directions x, y, and z of the axes of a system of rectangular cartesian coordinates which may not in general be assumed to be the directions of the principal axes of conductivity (i.e. those axes along which the directions of $\mathbf{v}$ and of grad ϕ coincide). A unit potential gradient in the x direction will produce a flow velocity with components $-K_{xx}\,\mathbf{i}$, $-K_{yx}\,\mathbf{j}$, and $-K_{zx}\,\mathbf{k}$, where the K's are conductivity constants characteristic of the medium. The subscript notation is similar to that of the strain tensor in the theory of elasticity. Similarly in response to unit potential gradient along y the flow velocity has components $-K_{xy}\,\mathbf{i}$, $-K_{yy}\,\mathbf{j}$, and $-K_{zy}\,\mathbf{k}$, and unit potential gradient along z causes flow with components $-K_{xz}\,\mathbf{i}$, $-K_{yz}\,\mathbf{j}$, and $-K_{zz}\,\mathbf{k}$. It follows that when the applied potential gradient is in the direction whose direction cosines are l, m, and n, the magnitude being F, i.e. when

$$\text{grad } \phi = F(l\mathbf{i}+m\mathbf{j}+n\mathbf{k}), \tag{2}$$

we have

$$\mathbf{v} = -F\left\{\begin{matrix} l(K_{xx}\,\mathbf{i}+K_{yx}\,\mathbf{j}+K_{zx}\,\mathbf{k}) \\ +m(K_{xy}\,\mathbf{i}+K_{yy}\,\mathbf{j}+K_{zy}\,\mathbf{k}) \\ +n(K_{xz}\,\mathbf{i}+K_{yz}\,\mathbf{j}+K_{zz}\,\mathbf{k}) \end{matrix}\right\} \tag{3}$$

which may be written* $\qquad \mathbf{v} = -\Gamma.\text{grad } \phi, \tag{4}$

where Γ is a dyadic whose nonion form is

$$\Gamma = \left\{\begin{matrix} K_{xx}\,\mathbf{ii}+K_{xy}\,\mathbf{ij}+K_{xz}\,\mathbf{ik} \\ +K_{yx}\,\mathbf{ji}+K_{yy}\,\mathbf{jj}+K_{yz}\,\mathbf{jk} \\ +K_{zx}\,\mathbf{ki}+K_{zy}\,\mathbf{kj}+K_{zz}\,\mathbf{kk} \end{matrix}\right\}. \tag{5}$$

Darcy's law for anisotropic materials thus takes the same simple form as for isotropic materials when conductivity is written as a dyadic; isotropy is a special case in which the magnitudes of all the dyads in (5) are zero with the exception of K_{xx}, K_{yy}, and K_{zz} which are all equal to K, the isotropic conductivity.

We seek to show, for the models we have selected, that there are three directions, which are mutually perpendicular, in each of which an application of a potential gradient produces a flow in that direction. It may be shown (Weatherburn, 1924) that this is so when the dyadic (5) is self-conjugate, i.e. when

$$\left.\begin{matrix} K_{xy} = K_{yx} \\ K_{xz} = K_{zx} \\ K_{yz} = K_{zy} \end{matrix}\right\}. \tag{6}$$

Our problem, then, is reduced to showing that the conductivity dyadic for the models chosen is self-conjugate.

* This use of the dyadic to express Darcy's law for anisotropic materials was brought to the author's attention by Mr. J. R. Philip. See also Hall, 1956.

The self-conjugacy of systems of fissures

If the conductivity of a material is the sum of a number of contributions due to n different sets of fissures and the conductivity dyadic of each contribution is separately self-conjugate, then the conductivity dyadic of the material as a whole is evidently also self-conjugate; for if the conductivity of the rth set is $\delta\Gamma_r$, where

$$\delta\Gamma_r = \left\{\begin{matrix} {}_rK_{xx}\,\mathbf{ii}+{}_rK_{yx}\,\mathbf{ji}+{}_rK_{zx}\,\mathbf{ki} \\ +{}_rK_{xy}\,\mathbf{ij}+{}_rK_{yy}\,\mathbf{jj}+{}_rK_{zy}\,\mathbf{kj} \\ +{}_rK_{xz}\,\mathbf{ik}+{}_rK_{yz}\,\mathbf{jk}+{}_rK_{zz}\,\mathbf{kk} \end{matrix}\right\}, \tag{7}$$

then

$$\Gamma = \sum_1^n \delta\Gamma_r. \tag{8}$$

From (5), (7), and (8) we have

$$K_{xx} = \sum_1^n {}_rK_{xx}$$

$$K_{yx} = \sum_1^n {}_rK_{yx}. \tag{9}$$

etc. etc.

Hence if $${}_rK_{xy} = {}_rK_{yx},$$

then $$K_{xy} = K_{yx}$$

and similarly for the other dyads. Hence if $\delta\Gamma_r$ is self-conjugate so is Γ.

We have said that when the conductivity of a system is self-conjugate we can find a set of three mutually perpendicular axes which have the property of coincidence of direction of potential gradient and consequent flow velocity. We now need to prove the converse, that a system with three mutually perpendicular principal axes is self-conjugate.

In a system of rectangular cartesian coordinates x, y, z, let the three mutually perpendicular principal axes have direction cosines L, M, N; l, m, n; and λ, μ, ν respectively where

$$Ll+Mm+Nn = 0, \tag{10}$$

$$L\lambda+M\mu+N\nu = 0, \tag{11}$$

$$l\lambda+m\mu+n\nu = 0. \tag{12}$$

Consider a potential gradient of magnitude F in a direction whose direction cosines are α, β, γ.

$$\text{grad}\,\phi = F(\alpha\mathbf{i}+\beta\mathbf{j}+\gamma\mathbf{k}). \tag{13}$$

This gradient may be resolved into components in the directions of the three principal axes thus:

$$\text{grad}\,\phi = F\left\{\begin{matrix} A(L\mathbf{i}+M\mathbf{j}+N\mathbf{k}) \\ +B(l\mathbf{i}+m\mathbf{j}+n\mathbf{k}) \\ +C(\lambda\mathbf{i}+\mu\mathbf{j}+\nu\mathbf{k}) \end{matrix}\right\} \tag{14}$$

where
$$\left.\begin{aligned} A &= \{\alpha(m\nu-n\mu)+\beta(n\lambda-l\nu)+\gamma(l\mu-m\lambda)\}/D \\ B &= \{\alpha(\mu N-\nu M)+\beta(L\nu-N\lambda)+\gamma(M\lambda-L\mu)\}/D \\ C &= \{\alpha(Mn-Nm)+\beta(lN-nL)+\gamma(mL-Ml)\}/D \end{aligned}\right\}. \quad (15)$$

In these expressions the denominator D is

$$D = \lambda(Mn-Nm)+\mu(Nl-Ln)+\nu(Lm-lM).$$

Let K_1, K_2, and K_3 be the hydraulic conductivities in the directions of the axes L, M, N; l, m, n; and λ, μ, ν, respectively. Then the velocity of flow in the system is $\mathbf{v}$ where

$$\mathbf{v} = -F\begin{Bmatrix} K_1 A(L\mathbf{i}+M\mathbf{j}+N\mathbf{k}) \\ +K_2 B(l\mathbf{i}+m\mathbf{j}+n\mathbf{k}) \\ +K_3 C(\lambda\mathbf{i}+\mu\mathbf{j}+\nu\mathbf{k}) \end{Bmatrix} \quad (16)$$

and this may be rewritten

$$\mathbf{v} = -F\begin{Bmatrix} \alpha(K_{xx}\,\mathbf{i}+K_{yx}\,\mathbf{j}+K_{zx}\,\mathbf{k}) \\ +\beta(K_{xy}\,\mathbf{i}+K_{yy}\,\mathbf{j}+K_{zy}\,\mathbf{k}) \\ +\gamma(K_{xz}\,\mathbf{i}+K_{yz}\,\mathbf{j}+K_{zz}\,\mathbf{k}) \end{Bmatrix} \quad (17)$$

after substitution for A, B, and C in (16). Comparing the expanded form of (16) with (17) we see that

$$\left.\begin{aligned} K_{xx} &= \{K_1 L(m\nu-n\mu)+K_2 l(\mu N-\nu M)+K_3\lambda(Mn-Nm)\}/D \\ K_{yy} &= \{K_1 M(n\lambda-l\nu)+K_2 m(L\nu-N\lambda)+K_3\mu(lN-nL)\}/D \\ K_{zz} &= \{K_1 N(l\mu-m\lambda)+K_2 n(M\lambda-L\mu)+K_3\nu(mL-Ml)\}/D \\ K_{yx} &= \{K_1 M(m\nu-n\mu)+K_2 m(\mu N-\nu M)+K_3\mu(Mn-Nm)\}/D \\ K_{zx} &= \{K_1 N(m\nu-n\mu)+K_2 n(\mu N-\nu M)+K_3\nu(Mn-Nm)\}/D \\ K_{xy} &= \{K_1 L(n\lambda-l\nu)+K_2 l(L\nu-N\lambda)+K_3\lambda(lN-nL)\}/D \\ K_{zy} &= \{K_1 N(n\lambda-l\nu)+K_2 n(L\nu-N\lambda)+K_3\nu(lN-nL)\}/D \\ K_{xz} &= \{K_1 L(l\mu-m\lambda)+K_2 l(M\lambda-L\mu)+K_3\lambda(mL-Ml)\}/D \\ K_{yz} &= \{K_1 M(l\mu-m\lambda)+K_2 m(M\lambda-L\mu)+K_3\mu(mL-Ml)\}/D \end{aligned}\right\}. \quad (18)$$

Confining our attention for the moment to K_{xy} and K_{yx} we find by eliminating N between (10) and (11) that

$$M(m\nu-n\mu) = L(n\lambda-l\nu). \quad (19)$$

Similarly eliminating n between (10) and (12) gives

$$l(\nu L-N\lambda) = m(\mu N-\nu M) \quad (20)$$

and eliminating ν between (11) and (12) gives

$$\mu(Mn-Nm) = \lambda(lN-nL). \quad (21)$$

From (19), (20), (21), and the expressions for K_{yx} and K_{xy} in (18) it follows that

$$K_{yx} = K_{xy}. \quad (22)$$

Similarly it may be shown that

$$K_{zx} = K_{xz}$$

and

$$K_{zy} = K_{yz}.$$

The conductivity dyadic is therefore self-conjugate, which was to be proved.

If a contributory conductivity has three mutually perpendicular principal axes it is therefore self-conjugate; and by virtue of (7), (8), and (9) so is the total conductivity of all such contributors, no matter how they may be oriented relative to each other. The total conductivity itself therefore has three mutually perpendicular principal axes. We do not discuss here how their directions may be found from a knowledge of the conductivities of the contributors. We may state the above findings in the following terms. If the conductivity of a material is the sum of a number of contributions each of which has three mutually perpendicular principal axes, then no matter how the contributors may be oriented relative to each other the total conductivity also has three mutually perpendicular principal axes.

We may now return to a consideration of the conductivity due to various sets of plane and doubly restricting fissures described in section 1. Clearly an infinite plane fissure has three mutually perpendicular principal axes, with zero conductivity normal to the plane and equal conductivities in any mutually perpendicular axes in the plane. A fissure which restricts flow to a specified direction is also characterized by three mutually perpendicular axes, with a finite conductivity in the direction specified and zero conductivity in any pair of mutually perpendicular directions normal to the specified direction. Hence any combination of any number and kind of such fissures results in a total conductivity which has three mutually perpendicular principal axes, in which directions a potential gradient and the resulting flow velocity coincide, so that conductivities characteristic of these directions may be specified in the ordinary scalar manner.

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NON-SYMBIOTIC NITROGEN-FIXING BACTERIA IN SOIL
III. TOTAL NITROGEN CHANGES IN A FIELD SOIL

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Summary

The total nitrogen content of a field soil was increased when rye grass or medic was grown on it, and also when cane sugar was added. Both grass and medic yielded substantial amounts of nitrogen in top material in addition to the soil nitrogen gains. With the grass treatment the increased nitrogen of the soil and the plant nitrogen together amounted to at least 165 lb. per acre over a 3-year period, and appeared to be the result of biological nitrogen fixation. It is concluded that the free-living nitrogen-fixing micro-organisms can make important contributions to the nitrogen economy of certain soils.

The probable inhibition of non-symbiotic nitrogen fixation by excessive soil aeration is discussed.

Introduction

INCREASES in nitrogen in legume-free soils have often been reported, for example Hall (1905), Smith, Thompson, Collier, and Hervey (1954), but the experimental data presented have seldom been such that an unequivocal claim could be made that non-symbiotic bacteria were responsible for the observed increases. In most cases it is possible that the increases occurred by concentration at the surface of soluble nitrogen from lower regions in the soil. Willis and Green (1948), working with pot soils planted to rice under flooded conditions, found increases in total nitrogen sufficient to compensate for nitrogen utilization by the plant and state that the increases were not due to algal growth. Their evidence is strongly suggestive of biological nitrogen fixation.

Attempts to gauge the nitrogen-fixing activity of the soil population have frequently been made by bacteriological methods and by soil incubation. Bacteriological examination of the soil, designed to count the number of clostridia and azotobacters present, had indicated that these organisms are seldom present in sufficient numbers to make a measurable contribution to soil nitrogen. This negative bacteriological evidence, discussed in previous publications (Parker, 1954*a*, 1955) has undoubtedly influenced subsequent thought and experimentation. For example, Theron (1951) did not measure total nitrogen changes in his field soils since '. . . accruals from this source (non-symbiotic bacteria) do not seem to be a material factor in the nitrogen relationships of soils'. Opposed to this are the findings of Parker (1954*a*, 1955) who concluded that the methods of counting nitrogen-fixing bacteria are completely inadequate and that, in the case of *Azotobacter*, even the distribution of this organism cannot be reliably determined. The latter conclusion is supported by the results of Kaila (1954), who showed that enrichment of soils before plating out led to a considerable increase in the number showing the presence of *Azotobacter*. Hutchinson (1918) incubated

soil mixed with straw in pots and showed small nitrogen increases. Jensen (1940) incubated similarly mixed soils in shallow plaques at different moisture levels and found small but significant increases in nitrogen, especially under saturated conditions. Laboratory incubation experiments of this kind are likely to be of limited use in evaluating the nitrogen contribution of the non-symbiotic bacteria, because of the absence of the growing plant.

Soils gain organic carbon, for the most part, from the growth and decomposition of plants *in situ*, and the living green plant is a powerful ecological factor in microbial processes. It enters into competition with the soil microflora for nutrients and oxygen; it carries a numerous rhizosphere population (Starkey, 1931, 1938); it may excrete organic substances into the soil (Loehwing, 1937; Rovira, 1955, priv. com.), and it stimulates intense microbial activity within the soil. Bartholomew and Clark (1950) found microbial activity to be roughly four times as great in cropped as in fallow soil, and the application of plant residues to have only a minor influence on activity in comparison with that exerted by the growing crop.

In a previous report (Parker, 1953) a comparison between virgin and adjacent cultivated soil (free of legumes) revealed a very highly significant increase in nitrogen and carbon in the cultivated soil. The annual increment of nitrogen, estimated at 15 lb. per acre, was regarded as biological in origin because of the very highly significant correlation between carbon and nitrogen which was demonstrated. Since the soil was sampled only from 0 to 4 in. deep, it is conceivable that the increased nitrogen in this layer was derived from deeper regions and concentrated at the surface by plant roots. The experimental results reported in this paper are from a field soil enriched with organic carbon from plant residues on the one hand, and from growing plants on the other. The soil was sampled at three levels to detect possible nitrogen movement in the profile.

Methods

Plot layout

From an area of land of uniform texture, a piece 144 ft. by 80 ft. was divided into 4 rows of 12 plots each 20 ft. by 12 ft. Four treatments were randomized on these plots giving 12 replications of each treatment. Samples were taken before treatment in late June 1952 from the 0–4, 4–7, and 7–10 in. levels; in early July 1953 from the 0–4 in. level only, and in August 1954 from the same levels as in 1952.

Sampling

Samples were taken with a 2-in. diameter steel tube, having a serrated cutting edge, a sliding depth indicator, and equipped with handles for turning. This tool was found to give good depth control with no mixing of soil from different depths. Six cores from each plot were bulked and mixed, the final sample being taken from the bulk sample into 1 lb.

screw-capped glass jars. Samples were dried in an air-draught oven at 52° C. immediately on return to the laboratory.

Total nitrogen determinations

Sample treatment. The soil sample was ground with a wooden pestle and mortar to break lumps and mix thoroughly, it was then quartered and sub-sampled to give about 50 g. for analysis. This was ground to pass a 0·5-mm. sieve. In 1952 and 1954 all macro-organic matter present in the soil was ground with the soil and was therefore included in the analyses.

Digestion. Duplicate 10-g. samples were digested by macro-Kjeldahl method after pre-soaking for ½ hour (Piper, 1947). The digestion mixture used was that of Willits, Coe, and Ogg (1949), and the digestion procedure finally adopted was 35 min. vigorous reflux after clearing, giving a total digestion time of 60–65 min. In recovery experiments from bulk samples of finely ground soil it was found that no significant differences in nitrogen yield occurred between 50, 60, and 70 min. digestion periods. The data presented by McKenzie and Wallace (1954, Tables 2 and 4) confirm that the mixture used in this laboratory could be expected to give full recovery after 60 min. digestion.

Distillation was performed in the Parnas Wagner apparatus; the distillate was absorbed in 2 per cent. boric acid solution, using the brom-cresol-green methyl-red indicator of Ma and Zuazaga (1942).

Reliability of recovery. The vigorous reflux caused considerable bumping of the digestion flasks, and it was considered that pyrolytic losses of nitrogen might occur. Therefore a recovery experiment was performed using 10 g. of ignited soil with 10 ml. of a solution of pure glycine added. The recovery from six replicate flasks was 99·44 per cent.

Twelve replicate 10-g. samples analysed from a bulk sample of Merredin soil, gave a mean yield of 0·0586 per cent. nitrogen with a standard deviation of ±0·00016. The analytical method used was therefore considered sufficiently reliable, in view of the much greater errors which occurred due to soil variability.

Nitrate recovery by Kjeldahl digestion. Nitrate in small amounts was recovered by the digestion method used. In an experiment with Merredin surface soil having a nitrate content of 22 p.p.m., no more nitrogen was recovered when salicylic acid was added to the digestion mixture. When a further 80 p.p.m. of nitrate-nitrogen was added to this soil, 68 per cent. of the added nitrogen was recovered. No modification of the digestion procedure was therefore deemed necessary to recover the small amounts of nitrate present in the experimental soil.

Nitrate nitrogen

Nitrate nitrogen was determined by the method used by Drover (1954) on the same samples as were used for total nitrogen and organic carbon analysis. In 1952 the nitrate content in p.p.m. nitrate-nitrogen was: 0–4 in., 21; 4–7 in., 12; 7–10 in., 9. In 1954 there were only 1–2 p.p.m. nitrate-nitrogen at all levels except in the sugar treatment, where 4–6 p.p.m. were present.

Organic carbon

Organic carbon was determined by the Walkley and Black wet-combustion method (Piper, 1947) and the results are presented for the 0–4 in. levels. Recoveries from 8 samples were plotted against dry combustion values. The regression was highly significant ($r = 0.9159^{**}$) and the recovery was about 70 per cent. of the total organic carbon.

Soil reaction was determined by glass electrode upon a 1:5 soil–water suspension.

Bacteriological examination. The soil was examined for the presence of *Clostridium* and *Azotobacter* by the methods described in previous publications (Parker 1954*a*, 1955). Both organisms were present.

Experimental

Plots were laid out on the Merredin Research Station 162 miles east of Perth in the autumn of 1952, to compare nitrogen and carbon changes occurring in soil when the organic matter additions to the soil came from growing plants on the one hand, and from plant residues on the other.

Soil. The soil chosen for the experimental site is grouped by Teakle (1938) in the Zone of Grey and Brown Calcareous, Solonized Soils of the low rainfall Eucalyptus woodlands. This soil type is important in the wheat-growing areas of Western Australia, and it usually carries a dense grass sward (*Hordeum leporinum*) when not being cropped to cereals. Some of the characteristics of the soil are given in Table 1.

TABLE 1

Some Physical Characteristics and pH of a Field Soil at Merredin Research Station

Depth	*pH*	*% by weight*			
		Coarse sand	*Fine sand*	*Silt*	*Clay*
0–4 in.	7·6	40·8	22·0	10·5	27·5
4–7 in.	7·9	32·0	16·7	12·5	40·0
7–10 in.	8·4	31·4	18·0	11·0	40·0

Cultural history. The virgin forest was cleared in 1909. Since that time the land had been cropped on fallow 13 times, had yielded a total of about 170 bushels of wheat per acre, and had received 11 cwt. of superphosphate per acre. It had been fallowed in the winter of 1951, and was ready for cropping again in 1952 when enclosed for this experiment. The soil may therefore be regarded as having reached a relatively stable state during forty years of cultivation.

Climate. The climate of the South-western Region of Western Australia has been discussed recently by Silsbury and Brittan (1955). The rainfall for the period of the experiment is given in Table 2.

Preparation of soil. The experimental area was cultivated several times with a small rotary hoe and finally raked to an even surface. The samples were taken from three levels after consolidation of the surface by light tamping.

TABLE 2

Monthly Rainfall in points (0·01 in.) at Merredin Research Station over a 3-year period

	Jan.	*Feb.*	*Mar.*	*Apr.*	*May*	*June*	*July*	*Aug.*	*Sept.*	*Oct.*	*Nov.*	*Dec.*	*Total*
1952	59	12	31	13	139	70	204	44	88	102	9	43	814
1953	3	26	374	158	279	222	185	129	46	59	42	0	1523
1954	6	4	0	28	289	54	237	158	68	53	14	11	922

Treatments were applied after the initial sampling. There were four treatments: (i) cane sugar and (ii) ground oat straw each at the rate of 3,000 lb. per acre; (iii) wimmera rye grass seed (*Lolium rigidum*, Gaud.), and (iv) barrel medic seed (*Medicago tribuloides*, Desr.) each at the rate of 20 lb. per acre. The sugar plots received no further addition; the straw plots received a further 3,000 lb. of ground straw in April 1954. The sugar and straw treatments were maintained free of plant growth by chipping off at the surface. The grass and medic plots received no further treatment, except that all legumes were removed from the grass plots. Superphosphate was applied in the autumn of each year to all treatments at 0, 90, and 180 lb. per acre. No significant differences due to phosphate were observed in the analytical results: this soil has shown a marked residual effect from previous superphosphate applications (Teakle and Cariss, 1943).

Sampling of plant tops. Plant growth was poor in 1952 due to an adverse season, but in 1953 very heavy growth of both rye grass and medic occurred. On 2 April 1954 all plant material on all plots was destroyed by fire, and the nitrogen contained in this material was lost to the atmosphere. In 1954 growth was again poor. The growth in 1952 and 1954, estimated at only 500–600 lb. dry matter per acre, was not sampled as its nitrogen content was negligible relative to the total nitrogen in the soil from 0–10 in. Samples of the 1953 growth were taken in July 1953 (before full flowering of either plant had occurred) with a 1 sq. ft. quadrat. The samples were oven-dried, weighed, and sub-sampled for total nitrogen analysis.

Results

The total nitrogen and organic carbon composition of the soil is presented in Tables 3 and 4. The 1952 means represent the initial fertility level of the soil, and may be taken as the basis for comparison of changes occurring in 1953 and 1954.

A significant increase in organic carbon occurred in the grass plot soil in 1953 ($p = < 0{\cdot}01$). By 1954 the organic carbon content of the medic and the straw plot soils had risen significantly ($p = < 0{\cdot}001$). The sugar-treated soil did not show a significant increase over the initial organic carbon content, but the straw-treated soil showed a substantial rise in 1954 in response to the recent application of straw. The time difference between the carbon changes in the grass and medic soils can be accounted for partly by the fact that macro root material was present

TABLE 3

Organic Carbon as % by weight of Soil from the 0·4-in. level. Means of 12 plots

Treatment	*1952*	*1953*	*1954*
Sugar . .	0·546	0·534	0·561
Grass . .	0·537	0·579	0·585
Medic . .	0·534	0·538	0·585
Straw . .	0·545	0·549	0·619

Least Significant Difference for means of 12:
5% = 0·029.
1% = 0·038.
0·1% = 0·049.

in such large and variable amounts in the 1953 soil samples that it was found necessary to sieve it out, and the grass roots being much finer and more numerous than those of the medic, tended to pass through the sieve in larger quantities. This may have allowed the grass soil to show a carbon increase one year earlier than the medic soil. Part of the increase in carbon under grass in 1953 may have occurred as the result of root excretion.

Table 4 shows a general upward trend in total nitrogen in all treatments at all depths. The only single depth to reach significance was the medic 0–4 in. which gained 0·003 per cent., although the grass 0–4 in. depth is approaching significance. When the data for the three depths of soil sampled (0–10 in.) are combined the increase shown for each treatment becomes significant at 5 per cent., the medic and grass soils approaching the 1 per cent. level of significance. That these individual increases are real is further supported by the fact that there was a nitrogen increase over the entire experimental area (from 0–10 in.) which was significant at the 0·01 per cent. level.

Plant nitrogen. The nitrogen content of the straw was determined and averaged 0·6 per cent. That added to the soil in the grass and medic seed was negligible.

Samples of rye grass and medic top material were taken in July at the same time as the soil was sampled, and dry weights and nitrogen contents were measured. The results are summarized in Table 5.

The yields quoted are at 5 per cent. fiducial limits, and show that a very large amount of nitrogen was present in the tops of the grass and medic. An examination of the rainfall data (Table 2) for 1953 and 1954 shows that the dry plant material would not have suffered losses by leaching before it was destroyed by fire. The roots of the grass were concentrated in the surface 2 in. of soil at the time of sampling, yet no depression of total nitrogen in the 0–4 in. level occurred.

Nitrogen balance sheet. Some explanation of the origin of the nitrogen in the tops of the grass is required, since there is no indication of loss of nitrogen from the soil. The medic results can be explained as due to symbiotic nitrogen fixation as the plants were effectively nodulated.

The volume weight of the experimental soil was not determined but

TABLE 4

Total Nitrogen as % by weight of Oven-dry Soil from the 0–4, 4–7, and 7–10-in. levels. Means of 12 plots

Depth of soil sampled	Treatments											
	Sugar			Grass			Medic			Straw		
	1952	1953	1954	1952	1953	1954	1952	1953	1954	1952	1953	1954
0–4 in. . .	0·0575	0·0574	0·0590	0·0555	0·0571	0·0580	0·0561	0·0569	0·0591	0·0566	0·0562	0·0585
4–7 in. . .	0·0401	..	0·0416	0·0404	..	0·0422	0·0402	..	0·0408	0·0402	..	0·0417
7–10 in. . .	0·0365	..	0·0383	0·0358	..	0·0378	0·0347	..	0·0372	0·0360	..	0·0384
0–10 in. . .	0·0460	..	0·0476	0·0451	..	0·0472	0·0449	..	0·0470	0·0455	..	0·0474

L.S.D. for means of 12 ($p = < 0·05$):

0–4 in. = 0·0028 per cent.
4–7 in. = 0·0027 per cent.
7–10 in. = 0·0026 per cent.

L.S.D. for means of 36 (0–10 in.) = 0·0016 per cent.

TABLE 5

Dry Weight and Total Nitrogen Content of Grass and Medic Tops in lb. per acre

	Dry wt.	% N	N *per acre*
Grass . .	9,530±1,913	1·3	124±25
Medic . .	7,033±1,350	3·16	222±43

it can be assumed with safety that for this soil, a silty clayey loam of poor structure, it would be at least 1·4 (Lyon and Buckman, 1943, p. 52) or 1·27 million lb. per acre 4 in. Taking 1·25 million lb. per acre 4 in. as a convenient figure, a nitrogen balance sheet for the experiment calculated from the soil nitrogen data (0–10 in.), plus the plant nitrogen, is presented in Table 6.

TABLE 6

Nitrogen Changes in lb. per acre including Soil and Plant Nitrogen

	Sugar	*Grass*	*Medic*	*Straw*
Gross changes in soil N, 1952–4	+50*	+65*	+65*	+58*
Less N added in treatments .	nil	< 0·5	< 0·5	36
Net increases in soil N . .	50	65	65	22
Nitrogen in plant tops . .	nil	99	179	nil
Net increases in soil and plant N .	50	164	244	22

* 50 lb. N per acre 10 in. is the least significant difference at 5 per cent.

From an examination of Table 6 the gain in nitrogen shown by the straw-treated soil can be seen to be due largely to the nitrogen contained in the straw. When this is subtracted the remainder is well below the 50 lb. of nitrogen per acre 10 in. which is required for significance.

The nitrogen in the plant tops shown in the two pasture treatments must not be confused with soil nitrogen, since the proportion which would normally become incorporated in the soil is not known. Nevertheless it represents a relatively large amount which, in the case of the grass, equals 7 per cent. of the total nitrogen of the soil to a depth of 10 in. A 3·5 per cent. change in total nitrogen is required to reach significance for this depth of soil, so that the nitrogen removed in the grass material, had it been derived entirely from the original soil nitrogen, should have appeared as a highly significant loss from the soil. Not only has there been no decrease, but there is a significant increase of 4·5 per cent. in soil nitrogen under grass. The data in Table 4 from the different depths sampled, 0–4, 4–7, and 7–10 in., indicate that the nitrogen contained in the grass tops has not been derived from the subsurface regions of the soil: there was no interaction between depths and treatments (V.R. = < 1).

Discussion

The total nitrogen content of a fine-textured soil increased when it was treated with cane sugar, or when rye grass or medic was grown upon it. The legume and the grass produced similar gains in soil nitrogen over 3 years, of the order of 60–70 lb. per acre 10 in., as well as large amounts of plant material in 1953. The nitrogen content of this plant material was equivalent, in the case of the grass, to about 100 lb. per acre.

The increases in soil nitrogen appear to be real increases, as there is no evidence of concentration at the surface from lower regions, and in any case the initial amount of mobile NO_3—N present in the soil was low. Nor do the observed increases appear to be due to any non-biological source or agency. Dhar (1943) claimed that cellulosic material mixed with soil, moistened and exposed to sunlight will fix nitrogen photochemically. Ingham (1950) claimed that under similar conditions ammonia may be absorbed from the atmosphere. But in our experiment the straw-treated soil, when allowance is made for nitrogen added in the straw, was the only one which did not show a significant gain in soil nitrogen. This treatment should have been well suited to test either Dhar's or Ingham's hypothesis, as the straw was incorporated into the surface inch of soil, where a considerable amount was exposed to sunlight and to the atmosphere. It seems probable, therefore, that the nitrogen increases observed in the legume-free soils were due to fixation by soil micro-organisms. When account is taken of the additional nitrogen removed from the soil in the form of rye grass tops, there can be little doubt that a very active biological fixation of nitrogen has taken place in this soil. Whether the micro-organisms responsible for the observed fixation consist principally of clostridia and azotobacters is impossible to say. The recent discovery of nitrogen-fixing yeasts (Metcalfe, Chayen, Roberts, and Wilson, 1954), and of nitrogen-fixation by *Aerobacter aerogenes* (Hamilton and Wilson, 1955) makes it legitimate to ask how many other soil microbes may be found to fix nitrogen.

The grass treatment shows a substantial total nitrogen increment in the form of plant and soil nitrogen (Table 6), an increment which, like that of the legume treatment, was largely associated with the growing plant. This result could be explained in three ways:

(i) The nitrogen was fixed by the non-symbiotic bacteria of the soil. For this it would be necessary to postulate that the soil organic matter under grass was metabolized at a much greater rate than in the sugar or straw treatments, as was shown to be possible by the experiment of Bartholomew and Clark (1950).

(ii) The nitrogen was fixed in the rhizosphere by micro-organisms utilizing root excretions. There is no clear evidence that this does occur with grasses, although Bukatsch and Heitzer (1952) have claimed rhizosphere fixation with peas.

(iii) The nitrogen was fixed by an endophyte as claimed by Brown (1933). There is still no support for Brown's early work. Indirectly, the conclusion of Hawker and Fraymouth (1951) that the endophytes of certain species of *Alnus*, *Myrica*, and *Hippophae*

are members of the lower fungi, does suggest that fungal endophytes may be able to fix nitrogen, as all these plants have since been shown to fix nitrogen symbiotically (Bond, 1955). The experimental data presented here can make no distinction between the suggested forms of nitrogen fixation but, whatever the explanation, it is clear that the growing non-leguminous plant has exerted a pronounced positive effect on nitrogen fixation in this soil.

Fine-textured soils of the type used in this experiment show fertility regeneration, judged by colour and vigour of crops, after periods under grass sward, and this phenomenon may now be explained as the result of biological nitrogen fixation. In Western Australia the coarse-textured soils do not show this benefit, possibly due to the inherently low fertility of such soils, but probably also to excessive aeration. Oxygen inhibits nitrogen fixation by the aerobe *Azotobacter* (Meyerhof and Burk, 1928; Parker, 1954*b*; Tschapek and Giambiagi, 1955), decreasing the amount of nitrogen fixed per unit of organic carbon metabolized, whilst *Aerobacter aerogenes* strains fix positive amounts of nitrogen only when they are grown anaerobically (Hamilton and Wilson, 1955). In addition, an aerobic environment precludes the growth of members of the genus *Clostridium*, many species of which can fix nitrogen (Rosenblum and Wilson, 1949). These organisms could play an important part in the nitrogen economy of some soils, for not only are they well distributed but they can fix nitrogen very much more efficiently than is usually supposed (Rosenblum and Wilson, 1950; Parker, 1954*a*). Restriction of oxygen diffusion into soil would therefore permit efficient utilization of organic materials by the aerobic organisms in the more oxidized zones of the soil, while allowing growth and fixation by the anaerobes in anaerobic zones or micro-environments.

It is interesting, in this context, to consider that most of the natural grass-growing areas of the world occur on soils of fine texture. Grass sward gives a dense mat of fine fibrous root material in intimate contact with the soil. The mechanical effect of roots in diminishing oxygen diffusion through soil pore spaces, combined with the respiration of the roots and their rhizosphere microflora, would together tend to cause an oxygen deficit in the soil water, and this may be important in allowing a wider range of nitrogen-fixing microbes to grow and fix nitrogen.

From the nitrogen balance sheet presented in Table 6, it appears that non-symbiotic nitrogen fixation could be of considerable importance in maintaining the nitrogen status of grassland soils.

The soil data presented and the microbiological evidence cited, together make a strong case for a reappraisal of the role of the free-living micro-organisms in the nitrogen economy of the finer textured soils.

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FEATURES OF NITRATE ACCUMULATION IN UGANDA SOIL*

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Summary

The accumulation of nitrate in unenriched tropical soil is not specially favoured by any stable moisture content between the limits of 15 per cent. and waterlogging. Change of moisture status during drying is accompanied by the appearance of much more NO_3 than under steady moisture conditions. Fluctuation of moisture status about an optimum average of 22–23 per cent. seems likely to provide the most favourable conditions.

The increase in NO_3—N occurs without equivalent loss in Kjeldahl-N, suggesting that ammonia for nitrification may be excreted from cells of a nitrogen-fixing system.

The biological operatives are highly resistant to drought, rapidly reviving in the presence of water, functionally related to a nitrogen-fixing system, responsive in some undefined manner to a soil-moisture content of 22–23 per cent., and insensitive to penicillin.

SEASONAL fluctuation in the amount of nitrate ion found in bare, unenriched soil is known to occur in a number of tropical and subtropical regions. It has been reported, for example, in the soils of Trinidad, South Africa, the Punjab and other regions of India, and in those of Australia and New Zealand.

Attempts have been made to relate the phenomenon to climatic factors, but there is little consistency in the results of such work. Rainfall (Hall, 1921, 1924), temperature (Russell, Jones, and Bahot, 1925), and insolation (Batham and Nigam, 1930; Rao and Dhar, 1931; Dhar *et al.*, 1933) have been separately and in combination invoked as the limiting factors. The amount of rainfall must obviously be important, but it is to the moisture status of the soil itself that nitrate values are likely to relate more closely.

Relationship between insolation and the nitrate status of soils has been claimed, on a basis of world data, by Batham and Nigam (1930) and by Dhar and his colleagues (1933). The latter suggest that sunlight, in the presence of mineral photocatalysts, brings about purely chemical changes leading to an increase in soil nitrate, but the work is open to criticism in that neither moisture, temperature, sterility, nor aeration is adequately controlled in the experiments described. In direct contradiction, Fraps and Sterges (1935) report that the effect of sunlight on nitrification is strongly inhibitory.

The contribution to soil nitrate deriving from electrical fixation during thunderstorms is very small compared to the quantities of NO_3 found in the soil during the large fluctuations which can occur within a single wet season. Recent work, however, indicates that atmospheric

* Part of work approved by the University of London for the award of the Ph.D. degree.

sources may be more considerable than rainfall analyses represent (Ingham, 1950; Dudlam, 1954; Angstrom and Hogberg, 1952).

Griffith and Manning (1949), working with soils near Kampala, Uganda, found an optimum soil-moisture content of 22·5 per cent. at which nitrate content tended to be highest. This was a tentative proposal and left much of the observed variation in results unaccounted for.

There is general agreement that the quantity of nitrate in a soil is much lowered under waterlogged conditions, but a definition of water conditions optimal for the accumulation of nitrate cannot be derived from a study of the literature. Greaves and Carter (1920) showed that for a wide variety of soils of America nitrate reaches maximum values at 50–60 per cent. of water-holding capacity. Albrecht (1922) found maximum NO_3 to occur at 14–18 per cent. (on an oven-dry basis). Gainey (1919) showed nitrification to increase up to the maximum moisture studied, i.e. 42 per cent. or saturation capacity, and is in agreement with Russell, Jones, and Bahot (1925) that maximum NO_3 and maximum moisture coincide, though the highest moisture used by the latter was 32 per cent. Hardy (1946) working with soils of Trinidad found the highest field nitrate values to occur at 13–14 per cent. when, during the dry season, soil moisture exceeded the wilting coefficient by only 3 or 4 per cent., whilst in Uganda Griffith and Manning found nitrate peaks to coincide with rainfall peaks unless there was leaching.

In contrast to these results is the work of Hall (1924) who associates high nitrate status in South African soils with intermittent light rainfall, of Hardy (1946) showing highest NO_3 values during periods of dryness after rain, of Albrecht and Uhland (1926) relating high nitrate status to successive air-drying and rewetting of the soil, and of Martin and Massey (1923) who found that in Sudan soils nitrate accumulated on the ridges of furrowed land but not in the troughs between ridges. In each of these instances the moisture values at the site of nitrification would be changeable.

There is yet little information about the microbiological basis upon which nitrate changes in tropical soils depend. The first approach to the problem in East Africa was made by Meiklejohn (1953) who showed that although the classical nitrifiers are present and active in Uganda soils, they do not wholly account for the pattern of fluctuation observed. In fact, the nitrifying performance of field soils in the laboratory was the reverse of expectations. Soils of high and increasing nitrate content in the field showed a lower nitrifying power in the laboratory than did soils whose field performance was poor.

Methods

(*a*) *Collection and preparation of material.* A large reserve of soils was collected initially and stored indoors. The rectangular plot from which the soil was taken had stood bare fallow for two wet and two dry seasons (12 months) receiving no treatment except weeding. It had, for some years previously, been used as a botanical-garden plot in which various species of indigenous grasses had been grown in tussocks. The plot measured 35 ft. by 8 ft. and was flat.

Twenty holes, 1 ft. square by 9 in. deep, were dug at random and the contents air-dried indoors. The dried soil was then put through a pair of sieves (meshes 14 and 36 per inch). The fraction collecting between the sieves was retained and the residue rejected. The material is a non-laterized red earth (Milne, 1936) and has been used in experiments over

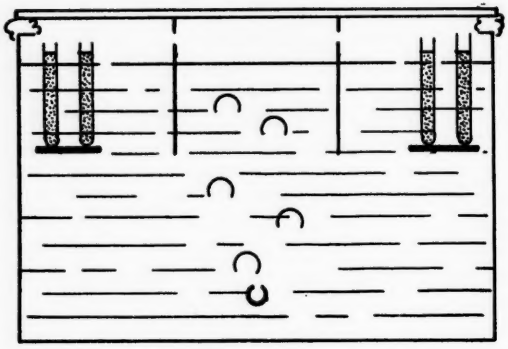

FIG. 1.

a period of more than 3 years. When fresh soil was required at one point the above process was repeated using topsoil (*c.* 9 in. layer) removed during building operations.

(*b*) *Final drying of the soil before experiments.* Vacuum-drying of a soil at room temperature can be made equivalent to oven-drying at 105° C. Drying for 24 hours at room temperature (desiccator temperature steady at 26° C.) at a pressure of 20 mm. Hg over fresh calcium chloride was adopted as standard procedure, a well mixed sample of soil from storage being placed in shallow ware dishes within the desiccator.

(*c*) *Maintenance of water status of soil and final form of apparatus.* Soil samples could be maintained in close approximation to any given water content equal to or greater than the maximum hygroscopic capacity in the following apparatus. A sheet-iron bath, 3 ft. by 2 ft. by 1 ft. 6 in. had perforated shelves fitted as shown in Fig. 1. A punctured brass tube led air to the bottom of the bath which was closed during experiments with a heavy wooden lid with a gasket of cotton wool. Two perforated splash-baffles were fitted to the lid. A stream of air bubbles from below served at once to stir the bath and maintain a constant atmosphere above the mouths of the tubes of soil which were carried on the shelves. Checks made during experiments showed some slight water loss over a period of 20 days, but this in no case exceeded 2 per cent. of water added. The water level was maintained 1·5 cm. below the mouths of the tubes.

When the water level was much reduced (e.g. 15 to 20 cm. below the rims of the tubes) there was a slow loss of moisture from the soil.

(*d*) *Preparation of test-tube units.* In the majority of experiments ordinary Pyrex test tubes, each numbered and of known weight, have

been used. These were filled to 1·5 cm. of the brim with dried soil (*c.* 17 g.).

A calculated quantity of distilled water was then added to the soil in each tube using simple 'drip funnels' which were made by twice drawing out lengths of glass tubing of 1 cm. bore to give fine-delivery capillaries. Moistened tubes were transferred at once to the bath.

Moisture is expressed throughout these experiments as per cent. by weight of dry soil.

(*e*) *Nitrate determination.* The phenoldisulphonic-acid method was used (Frederick, 1919; Piper, 1944) and estimations made in quadruplicate. Blank determinations were carried out at intervals and were invariably nil.

(*f*) *Kjeldahl nitrogen determinations.* Determination of nitrogen other than nitrate (and nitrite, if present) was made by the Kjeldahl method as described by Piper (1944). Estimations were made in quadruplicate. Blanks were determined for each batch of reagents used, but gave nil results.

Kjeldahl nitrogen and NO_3 were determined in parallel groups of tubes, to one set of which a known quantity of nitrate was introduced and the results confirmed that for the conditions of these experiments the ordinary Kjeldahl did, in fact, neglect nitrate.

Experimental

1. For each of the soils used in these experiments field capacity has been measured as 25 per cent. and permanent wilting coefficient as 12·5 per cent.

2. In attempting to determine whether a single moisture optimum exists for nitrate accumulation experiments were carried out in which the course of nitrate change was followed in sets of soil tubes provided with 15, 20, 25, 30, 35, 45, and 55 per cent. water on a dry-soil basis. The tubes were incubated in the bath already described. Temperature remained constant at $24 \pm \frac{1}{2}°$ C., aeration was at a constant rate (*c.* 1 litre per minute) and light was excluded.

Nitrate was determined at daily intervals in quadruplicate for each series of tubes. In the 45 per cent. and 55 per cent. series the figures obtained could only be regarded as maximum possible values. In nearly all tubes with 45 per cent. and in all with 55 per cent. water accurate determination of NO_3 could not be made by the technique used because of the very low colorimeter readings obtained.

The curve for 15 per cent. moisture shows a marked initial lag behind others (Fig. 2), but finally the same plateau is reached as in subsequent series. In other experiments this plateau has been maintained for as long as 25 days under steady moisture conditions. A single curve represents the changes found, but the points for each set of tubes are separately identified. At 45 per cent. and 55 per cent. moisture nitrate is much depressed and the points plotted indicate estimated values only.

The nitrate content of stored soil which had remained dry in the laboratory during 18 months showed no change, being stationary at 6 p.p.m. NO_3—N throughout the period. It contains approximately

10 per cent. moisture. After a further 30 months its NO_3—N content was 7 p.p.m.

There is thus a lower limit of moisture below which significant NO_3 increase does not occur. It is not closely defined but, for this soil, lies between 10 and 15 per cent.

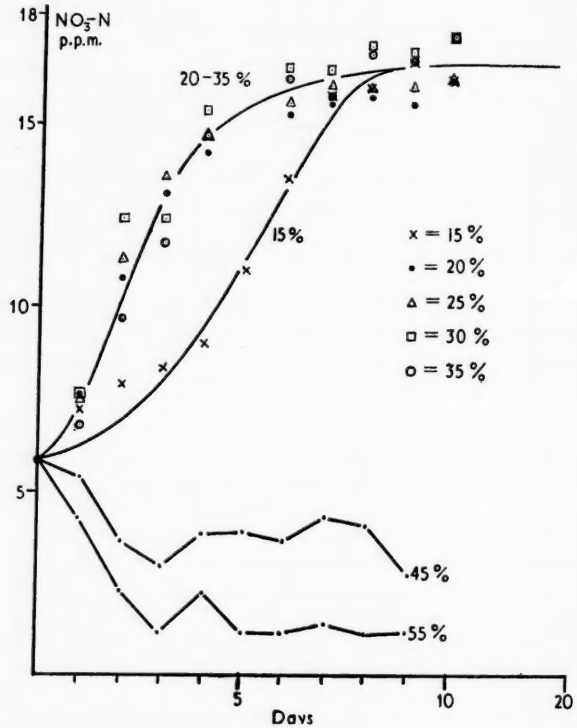

FIG. 2.

No steady moisture value over the range between 20 per cent. and 35 per cent. is more favourable than others for the enhancement of nitrate status. Whatever the agent of the process it is uninfluenced by the water content of the soil between these limits.

Another experiment made in the same way but using sets of tubes moistened to 18, 20, 22, 24, and 26 per cent. and maintained without loss of water gave similar results.

Observations relating to waterlogging showed that in the 45 per cent. tubes waterlogging extended through almost the entire column and in several cases a water-seal appeared above the soil surface. In some tubes where no water-seal developed enough nitrate was found to allow colorimetric measurement to be made with ease, but in no instance where a seal appeared did measurable quantities of nitrate occur. Columns

with 35 per cent. moisture were also waterlogged at the bottom of the tubes, but in no case did this have any effect on nitrate status or upon the rate of accumulation of NO_3.

3. The distribution of water within soil columns of the 15 per cent. series was irregular, and similar conditions may prevail in other sets of tubes. Nitrate measurements made on tubes in this state may merely provide a mean value representing widely different conditions from point to point in the soil mass, whilst the real effect of moisture status is obscured.

An experiment made to test this possibility was carried out using tubes 15 cm. in length and 3·5 cm. in diameter. One end of each tube was stoppered by a 'melted-in' plug of paraffin wax and beeswax. A set of 40 tubes was filled with dried soil to a depth of 10 cm. and a measured quantity of water added to give 26 per cent. moisture. By means of slight pressure the wax plugs could be dislodged and thrust upwards so as to push out the soil column. Soil could then be removed in layers 1 cm. deep and the nitrate or water profile described by determinations at successive levels. The tubes were divided into two sets and placed in the metal tank and the water level lowered below the bases of the tubes. Conditions were otherwise as before and daily estimations of NO_3 and moisture were made in duplicate by 1 cm. layers from the top of tubes to the bottom. The duration of the experiment was 9 days with a set of nitrate values after 27 days.

A second-order regression curve fitted to the results of this experiment (Tables 1(*a*) and 1(*b*)) shows a probable optimum moisture value at 22·5 per cent. (cf. Griffith and Manning, 1949). There is, however, much unaccounted variation (t max. = 6·17; P quadratic < 0·001). The general effect is again to emphasize the wide range of moistures in which nitrate can accumulate rather than to distinguish a specially favourable value.

There is some water loss from the tubes which accounts for the accumulation in the upper layers. A curious point is that in the later stages columns are driest at the bottom and appear to be losing water from below upwards.

4. The failure of any distinct and unmistakable moisture optimum to emerge in the foregoing experiments directs attention to the effect of changing moisture status, and experiments were designed to follow nitrate changes in tubes losing water at a slow rate by evaporation. For this purpose a series of tubes was prepared with 25 per cent. added moisture and fortnightly determinations of NO_3 and water made over a period of 14 weeks.

Fig. 3 shows an approximately sevenfold increase in NO_3—N. This large change proceeds in two steps, a sharp inflexion in the curve appearing between the 4th and 6th weeks. It is striking that this occurs at 22–23 per cent. moisture, a value which in view of previous findings assumes additional interest. The reduction in the rate of nitrate production is accompanied by a pause in the loss of water.

This experiment was carried out using soil which had been stored in the laboratory for 3 years. The whole process was, however, repeated

TABLE 1

Profiles of (a) NO_3—N in p.p.m. and (b) moisture (% oven-dry soil) through soil columns

Cm. depth	Days										
	0	1	2	3	4	5	6	7	8	9	27
(a)											
0–1	< 5	< 5	< 6	6	9	11	10	15	14	15	30
1–2	< 5	< 5	< 5	< 6	10	11	11	11	13	15	27
2–3	< 5	< 5	< 5	< 6	8	10	11	12	13	14	24
3–4	< 5	< 5	< 5	< 6	11	11	11	14	14	15	18
4–5	6	< 5	< 5	8	12	12	13	12	14	15	20
5–6	< 5	< 6	< 5	7	12	14	13	12	15	16	16
6–7	< 5	< 6	< 5	6	12	16	13	13	15	15	12
7–8	5	6	6	10	13	15	11	13	14	12	12
8–9	6	< 6	7	6	14	12	11	9	14	9	< 5
9–10	11	7	15	10	11	6	5	6	5	5	0
(b)											
0–1	31	27	27	28	23	26	25	25	25	25	..
1–2	30	22	27	28	23	26	22	25	24	25	..
2–3	31	27	24	27	24	24	26	24	24	26	..
3–4	29	28	28	27	26	27	26	25	25	25	..
4–5	29	27	26	28	26	27	26	25	25	25	..
5–6	29	26	22	24	24	29	26	23	24	24	..
6–7	26	24	30	17	25	27	25	22	23	22	..
7–8	25	25	25	24	25	24	24	22	22	21	..
8–9	22	23	20	23	22	23	23	22	22	21	..
9–10	19	24	24	22	22	24	30	19	21	21	..

using a fresh sample of soil collected as before. The curve obtained was similar in all respects with that obtained with the old soil, the identity extending into the latter part of the graph where NO_3 fluctuated in a similar way.

5. During the latter experiments parallel measurements of Kjeldahl nitrogen were also made. If the appearance of large amounts of nitrate-N accompanies an overall increase in soil nitrogen a problem of great interest may develop depending upon how the changes in nitrate-N and total-N prove to be related.

(i) A set of tubes was prepared, NO_3—N and Kjeldahl-N being determined at the outset and, finally, at the end of 90 days' incubation. Results are given in full in Table 2.

The figures show no significant change in Kjeldahl-N, but an obvious increase in NO_3—N. A comparison of arithmetic means shows an increase of some 5 per cent. total nitrogen. This is entirely due to a rise in the quantity of nitrate.

(ii) Enough tubes were prepared to allow quadruplicate determinations of Kjeldahl-N to be made at fortnightly intervals over a period of 14 weeks. In Fig. 3 Kjeldahl-N shows a consistent rise to about the 8th week with a tendency to fall again towards the end of the experiment. The total-N increase is of the order of 10 per cent.

(iii) A similar series was prepared using fresh soil. The change in Kjeldahl-N differs from that found in the old soil preparations, the main feature of the graph being the sharp fall between the 6th and 8th weeks when nitrate-N is rising strongly. There is again an apparent increase in total nitrogen of 2–3 per cent.

TABLE 2

Kjeldahl-N and NO_3*—N before and after 90 days' incubation during slow drying*

	Initial	*After 90 days*
Kjeldahl-N .	912	940
	925	923
	960	910
	900	928
	930	938
	960	lost
NO_3—N .	7	59
	7	55
	7	55
	7	58
	7	55
	7	46

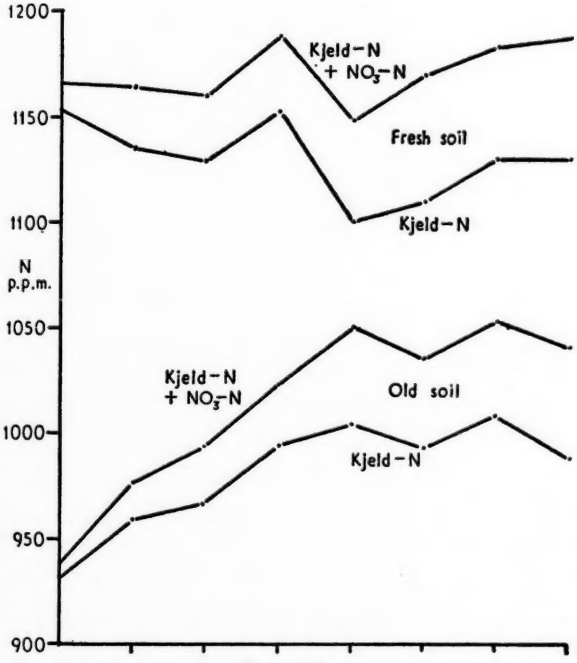

FIG. 3 (*a*).

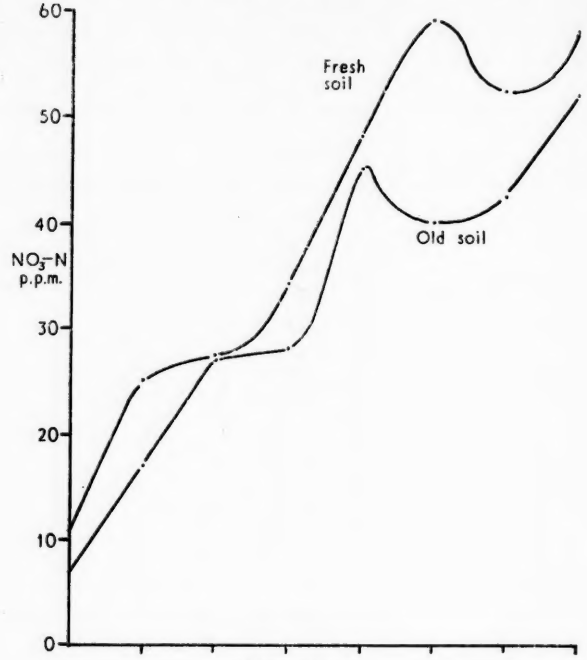

FIG. 3(*b*).

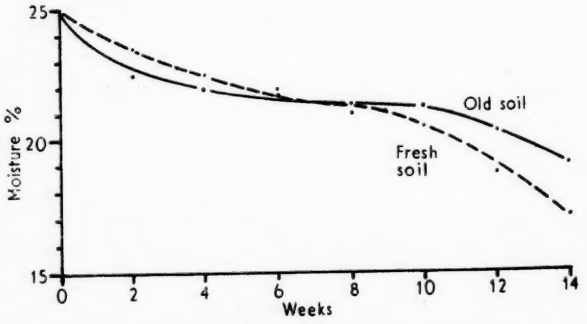

FIG. 3(*c*).

6. *Biological nature of the nitrate-producing agency.* The nitrate status of tubed soil was followed in four parallel series of tubes (*a*) containing dried soil with 25 per cent. of sterile distilled water, (*b*) previously sterilized soil (180° C. for 5 hours) with 25 per cent. sterile distilled water, (*c*) dried soil with 25 per cent. of a solution of formalin (5 per cent.), and (*d*) dried soil with 25 per cent. of a solution of penicillin (5,000 units per ml.). Nitrate changes upon incubation in the metal

tank are summarized in Fig. 4, and show that only in the control and in the presence of penicillin did any increase occur. The prevention of biological processes in (*b*) and (*c*) is accompanied by the complete loss of the nitrate-producing property.

Any photocatalytic process is impossible since, in addition to the bath

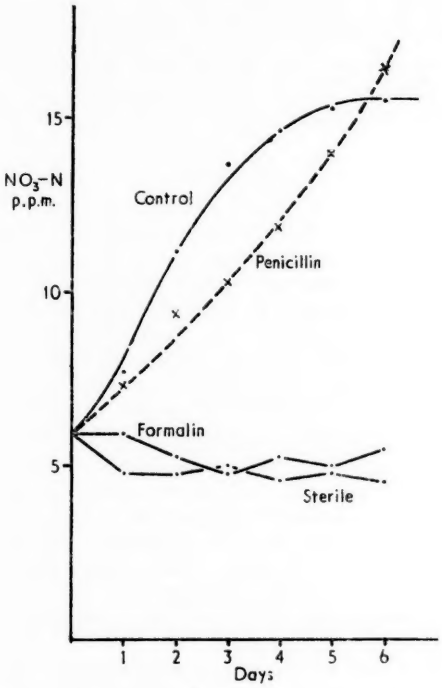

FIG. 4.

being completely closed and in darkness during daytime, the further precaution was taken of removing tubes in the dark after nightfall.

The novel idea of the interception, by suitable adsorbing surfaces, of mineral nutrients (including NO_3—N) occurring in particulate form in the atmosphere is examined by Ingham (1950), but the extent to which such a process might contribute to the nitrate content of soil in experiments such as the present is doubtful. The effect of oven-sterilization on adsorbing surfaces may be profound and may account, in part, for the failure of soil treated in such a way to acquire mineral substances from the air, but the differences in results obtained from the control, formalin, and penicillin series can hardly be accounted for in similar terms. Furthermore, the quantitative changes in NO_3 which occur in these and in previous experiments appear to exceed what could be expected to arise from atmospheric sources.

Only when microbiological processes are permitted does nitrate status improve and the conclusion that the process is biological is specially reinforced by the alteration of the pattern of accumulation caused by the addition to the soil of a biological differential in the form of penicillin. Penicillin is inhibitory or lethal to many soil organisms, but not to the agents bringing about nitrate formation.

An observation made during this experiment was that in those tubes where NO_3 status improved (i.e. in control and penicillin series) the surface of soil aggregates was glossy and mucoid in appearance as compared with those in which nitrate value did not increase. In the latter, soil crumbs remained matt-surfaced and without highlights.

Discussion

Moisture content and nitrate status. Between the roughly defined limits of air-dryness (10–15 per cent. moisture) and waterlogging (*c.* 45 per cent. moisture) there is a broad range of soil-moisture conditions under which, in these experiments, quite large quantities of nitrate appear in the soil. The failure of any well-defined optimum to emerge may be interpreted in two ways: either it is so limited as not to have been achieved by the techniques used, or it does not exist.

Evidence has been given showing how variable are the conditions in soil columns, and if the hypothetical moisture optimum represents a sensitive and highly unstable condition it may not have been produced except transitorily in small zones within the soil mass. If, on the other hand, no optimum exists the only other possibility is that nitrate production occurs in response to *change* of moisture status. The recurrence of a moisture value of 22–23 per cent. in experimental contexts of different type is best interpreted in this light. The statistic derived from results in experiment 2 might equally well have arisen if the *oscillation* of moisture status about a mean of 22·5 per cent. were the most favourable condition for nitrate accumulation.

The depression of nitrate status by waterlogging is probably of slight importance under agricultural conditions where drainage is efficient and the major cause of loss of nitrate from the soil must be leaching (Smith, 1928). An incidental demonstration of the powerful effect of downward movement of water is given in the first column of results in Tables 1(*a*) and 1(*b*) where, although only a small fraction of the total water has percolated to the bottom of the profile, the bulk of the nitrate present has been carried into the lower 2 or 3 cm. of soil.

Characteristics of the microbiological agency

1. The nitrate productivity of the soil, stored dry in the laboratory for three years, is almost unimpaired, and the organisms involved in nitrate production must be robust forms capable of withstanding long drought. This is known to be true of the classical nitrifiers, *Nitrosomonas* and *Nitrobacter*.

2. In Fig. 2 the curve shows no sign of a prolonged lag-phase and, should the nitrate-producers be capable of growth on culture media

similar in nutrient content to their native soil, they should be represented amongst the first crop of colonies to appear on suitable plates with soil inocula.

The plateau of the same curve continues uninterrupted for as long as 25 days. Either the nitrate is used at the same rate as it is being produced or it is not utilized. The occurrence of growth processes is shown by the appearance, between the 7th and 10th days, of a luxuriant crop of Zygomycete sporangia in some of the tubes, but this has no observable effect on the amount of nitrate to be found.

3. There is close similarity between the nitrate curves for old and for fresh soil though the Kjeldahl- and total-N graphs differ markedly in important respects. The nitrate curve for either soil material may be considered in three parts (i) an initial steep rise ending in a sharp inflexion at a nitrate level of 25–30 p.p.m., (ii) a further steep rise to a marked peak, and (iii) a fall with subsequent recovery at the end of the experiments.

The inflexion separating (i) and (ii) occurs during a pause in the loss of water and, whatever the cause of this, the microbiological complex reacts to it as shown by the change in the rate of nitrate production.

4. There can be little doubt that the increase in total soil nitrogen consistently appearing in these experiments is real and that a process of nitrogen fixation is occurring. The increase, moreover, is entirely in the form of extra nitrate.

Since there is no equivalent overall loss in Kjeldahl-N, processes must be occurring by which ammonia is provided from sources other than the breakdown of amino acids or proteins. The interesting possibility thus arises that ammonia for nitrification is being excreted by organisms themselves fixing nitrogen.

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A REVIEW OF TRACER STUDIES IN SASKATCHEWAN ON THE UTILIZATION OF PHOSPHATES BY GRAIN CROPS*

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Summary

The use of P^{32} as a tracer has been particularly valuable in studying the uptake of phosphorus from fertilizer and soil. It is a technique which may be used to differentiate between the availability of phosphorus in both soils and fertilizers.

The work was done on soils well supplied with lime. The fertilizer was drilled with the seed unless otherwise stated.

Results show that the wheat plant obtains most of its phosphorus from the fertilizer in the early stages of growth. The proportion obtained from the soil increases rapidly after the fourth week. Most of the phosphorus in the above-ground part of the plant migrates to the head of the plant as it matures.

Increasing the rate of application of the fertilizer results in a decreased utilization of soil phosphorus with a proportional increase in uptake of fertilizer phosphorus. The availability of phosphorus varies greatly in different carriers. Under the soil and climatic conditions to which the data apply mono-ammonium phosphate had superior availability to calcium phosphates. Di-calcium phosphates are relatively lower in availability than mono-calcium phosphates. The availability of fertilizer phosphorus can be increased through the incorporation of small quantities of sulphur in the material. In drier areas at least the phosphatic fertilizers appear to be most effective when placed close to the seed. Under drought conditions a larger proportion of the phosphorus utilized by the plant comes from the fertilizer. Increased yields may result from the application of phosphates even under extreme drought conditions.

Certain varieties of barley respond better to phosphatic fertilizer than do others. This differentiation did not appear in the wheat and oat varieties tested.

The effect of different levels of radiation on plant growth and uptake of phosphorus has been studied in considerable detail. Deviations in results caused by radiation are considered unlikely to affect the type of experiments reported in this paper.

FIELD experiments in which P^{32} was used as a tracer in studying the uptake of soil and fertilizer phosphorus by spring wheat were first undertaken at the University of Saskatchewan in 1946. Since that time field and greenhouse experiments with wheat and other grains have been carried on each season, and a considerable amount of data accumulated. It is the purpose of this paper to review briefly the more important conclusions reached in these experiments and to present also some of the data necessary in support of such conclusions.

Uptake of Soil and Fertilizer Phosphorus by Wheat at Various Stages of Growth

Greenhouse experiments (Spinks and Barber, 1948) indicated that there is greater utilization of fertilizer phosphorus than of soil phosphorus in the earliest stages of growth of the wheat plant. In these experiments the fertilizer was applied in solution in the region where the seed was

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† Deceased 21 November 1955.

planted. The rate of uptake of fertilizer phosphorus reaches a maximum at 2–6 weeks and begins to fall off as the plant reaches the heading stage at about 8 weeks. On the other hand, the rate of uptake of soil phosphorus increases rapidly in the 4–6-week period and at this stage reaches a rate of uptake nearly three times as great as the uptake of fertilizer phosphorus (Fig. 1). After the heading stage the proportion of fertilizer

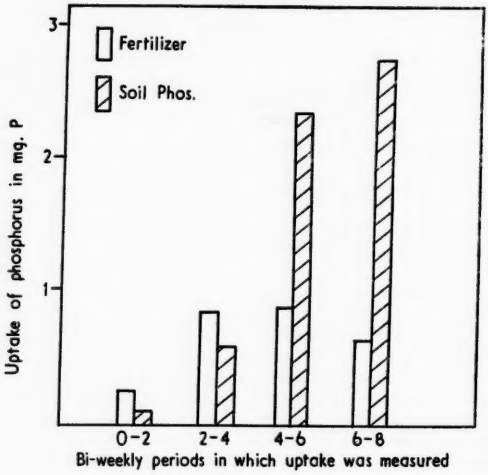

FIG. 1.

phosphorus utilized is sharply reduced, but a considerable amount of phosphorus is obtained from the soil until maturity (Dion *et al.*, 1950) (Table 1). The data given in Table 1 also illustrate the great difference in availability of the phosphorus in two carriers bearing similar ratios of nitrogen to phosphorus and applied at the same rate of P_2O_5 per acre.

TABLE 1

*Cumulative Uptake of Fertilizer and Soil Phosphorus by Wheat at various Stages of Growth with a Comparison of Two Phosphate Fertilizers**

24 lb. P_2O_5 *per acre*	*4 weeks (9–10 in.)*		*7 weeks (heading)*		*9 weeks (soft dough)*		*13 weeks (mature)*		*Grain yield (g.)*
	Total P (mg. P)	*Fert.* P	*Total* P (mg. P)	*Fert.* P	*Total* P (mg. P)	*Fert.* P	*Total* P (mg. P)	*Fert.* P	
Mono-ammonium phosphate (11–48–0)	27·0	12·5	177·2	75·5	195·0	77·0	281·0	101·0	78·0
Di-calcium phosphate plus calcium nitrate (8–30–0)	19·7	1·9	126·1	15·1	182·0	19·0	241·0	22·0	63·3
Unfertilized	18·8	..	95·0	..	146·0	..	188·0	..	49·0

* Data from field trials at Birch Hills, Sask. 1948. Figures are averages of four replicates of a 6-ft. row.

The pattern of uptake of fertilizer and soil phosphorus illustrated in Fig. 1 and Table 1 has been consistent throughout these experiments. In the early stages of growth the wheat plant obtains the larger proportion of its phosphorus from the fertilizer but later on by far the greater

amount is obtained from the soil. The fact that the fertilizer was placed close to the seed and so concentrated in a volume of soil which is comparatively small compared to the volume ultimately exploited by the roots of the plant no doubt favoured early utilization of the applied phosphorus. Applications of the phosphate fertilizer at later stages of growth may result in a great uptake of the fertilizer phosphorus, but apparently is much less effective in increasing yields than when the fertilizer is applied at seeding time (Dion Spinks, *et al.*, 1949).

The phosphorus content of the tissue of the wheat plant is higher in the earlier stages of growth and lessens towards maturity. As maturity approaches phosphorus migrates to the head of the wheat which eventually contains 75 per cent. or more of the fertilizer phosphorus utilized (Barber, 1947).

Effect of Rate of Application on Uptake of Soil and Fertilizer Phosphorus

The uptake of fertilizer phosphorus and of the total phosphorus utilized by the plant was determined by separate analyses. The latter was determined by direct determination of total phosphorus in the plant material. The fertilizer phosphorus was determined by measuring the radioactivity in either the precipitated phosphates or by the use of the hollow-cylinder method of direct determination of P^{32} in the plant material (Spinks and Barber, 1947; Kristjanson *et al.*, 1951). The soil-phosphorus uptake is calculated by subtracting fertilizer phosphorus taken up from the total phosphorus in the plant. If the total phosphorus minus the fertilizer phosphorus should indicate a soil-phosphorus uptake greater than the amount of uptake on the unfertilized plot, there would be evidence that additions of phosphate fertilizer had stimulated the uptake of soil phosphorus. This appeared to be the case in some early greenhouse experiments using tracer phosphorus (Spinks and Barber, 1948) and it was suggested that this might occur especially where only low rates of fertilizer were applied. Subsequent greenhouse work failed to confirm this result (Spinks and Barber, 1948). Results obtained from two field experiments in 1950 (Fig. 2) indicated a steady decline in uptake of soil phosphorus as the application of fertilizer was increased beginning with a low rate of 6 lb. P_2O_5 per acre and reaching as high as 96 lb. P_2O_5 per acre.

The uptake of fertilizer phosphate increases fairly steeply with increasing increments of fertilizer up to about 24 lb. per acre P_2O_5. From this rate up to the highest rate used (96 lb. P_2O_5) the increased uptake is less pronounced (Fig. 2). Total-phosphorus uptake and grain-yield data follow the same general trend, both yield and uptake rising with increasing rates of application. However, lower rates are relatively more effective than higher rates in increasing both yield and total uptake. In these data soil-phosphorus uptake decreased rather uniformly as the application of fertilizer phosphorus was increased.

When data such as that from which Fig. 2 was compiled are used to plot application of P_2O_5 against the ratio P-from-fertilizer/P-from-soil, it is found that a straight-line relationship exists. The slope of this line

gives a measure of available soil phosphorus in terms of the fertilizer used (Mitchell *et al.*, 1952). This relationship has been pointed out previously by Fried and Dean (1950) and Larsen (1950).

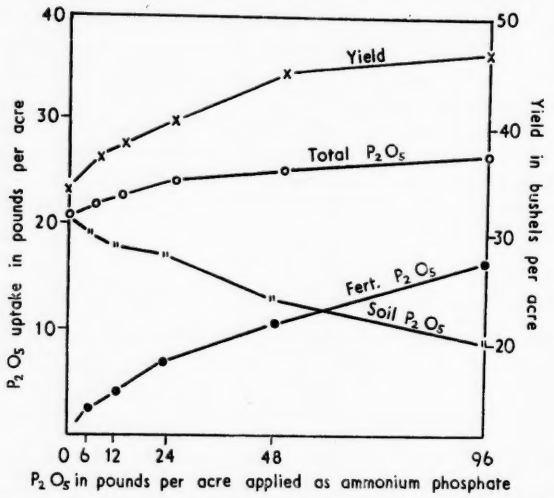

FIG. 2. Influence of increasing increments of P_2O_5 on yield and uptake of soil and fertilizer phosphorus by wheat.

Availability of Phosphorus in Various Phosphate Fertilizers

The agricultural soils of Saskatchewan are generally well supplied with lime. The soil reaction is commonly near neutral although acid soils are occasionally encountered. There are significant areas of highly calcareous soils, and reactions as alkaline as pH 8·0 may occur in such soils.

Field tests using several phosphate fertilizers had already indicated that mono-ammonium phosphate was a more efficient carrier than calcium phosphates such as superphosphate or triple superphosphate. Since the tests were on fallow-land crops, it seemed unlikely that the nitrogen in the ammonium phosphate was having a direct effect on growth. In this region fallowed land accumulates considerable amounts of nitrate nitrogen during the fallow period, and loss by leaching is very small (Larson and Mitchell, 1939).

It was of great interest, therefore, to test the uptake of fertilizer phosphorus from a number of carriers likely to exhibit varying degrees of availability, especially since the use of phosphates had only recently become a common practice in this area.

The fertilizers tested were mono-ammonium phosphate, mono-sodium phosphate, mono-calcium phosphate, di-calcium phosphate, and di-calcium phosphate plus calcium nitrate. The basic rate used for all fertilizers was 24 lb. P_2O_5 per acre. The ammonium phosphate was also applied at half this rate and at a double rate, i.e. 12 and 48 lb.

P_2O_5 per acre. The experiment was carried out in 1948 at two locations. The average result of the two tests is shown graphically in Fig. 3 (Dion, Dehm, *et al.*, 1949; Dion *et al.*, 1950).

The general superiority of ammonium phosphate and the poor response obtained from di-calcium phosphates are well illustrated in Fig. 3. Sodium phosphate and mono-calcium phosphates appear to be intermediate in availability. These results are in agreement with data from earlier field tests which also illustrate the superiority of mono-ammonium phosphate as a phosphatic fertilizer for the soils of the region (Mitchell, 1946).

There is no significant difference in uptake of soil phosphorus between treatments, but the fertilizer-phosphorus uptake is higher for the basic and double rate of ammonium phosphate, and for sodium and mono-calcium phosphates than for either of the di-calcium-phosphate treatments. Similarly, the three first-mentioned fertilizers show significantly higher total uptake of phosphorus over di-calcium phosphorus although only the basic and double rates of ammonium phosphate give significantly higher values than those for di-calcium phosphate plus calcium nitrate. These statements may also be applied to the yield data in which the basic and double rates of ammonium phosphate and the sodium and mono-calcium phosphates are significantly better than di-calcium phosphate, but only the basic and double rates of ammonium phosphate significantly outyield di-calcium phosphate plus calcium nitrate. Neither di-calcium phosphate or di-calcium phosphate plus calcium nitrate, nor the half-rate of ammonium-phosphate treatments gave significantly better yields than the unfertilized plot.

It is evident that there is a great variation in the efficiency of phosphate carriers for the crops and soils studied. In general, it appears that the less calcium there is in the fertilizer the more efficient it is likely to be in supplying phosphorus to the crop and so in producing increase in yield. A greenhouse experiment (Dion, Spinks, *et al.*, 1949), gave similar results to the above in a comparison of the efficiency of ammonium, mono-calcium, and tri-calcium phosphates as a source of fertilizer phosphorus for wheat.

In an experiment hitherto unreported di-ammonium phosphate proved equal in efficiency to mono-ammonium phosphate.

The Effect of Small Additions of Sulphur in Increasing the Availability of Phosphorus in Fertilizers

The possibility of a di-calcium-phosphate and calcium-nitrate fertilizer of 8–30–0 analysis appearing on the market was responsible for a special interest in the availability of the phosphorus in this carrier. The incorporation of small amounts of sulphur with the fertilizer was tried as a means of improving the availability of di-calcium phosphate as compared to mono-ammonium phosphate.

Greenhouse work gave very encouraging data indicating that 5 per cent. sulphur added to an 8–30–0 di-calcium phosphate would improve the availability and uptake of phosphorus to equal that of the more

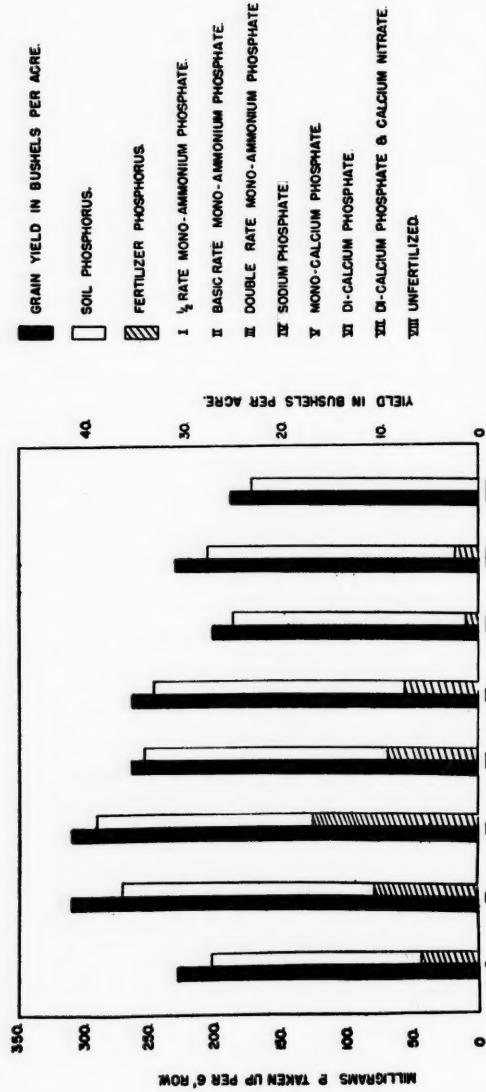

FIG. 3. Variations in availability of phosphate in several carriers as indicated by yield response and uptake of phosphorus (basic application 24 lb. P_2O_5 per acre).

available ammonium phosphate (Table 2). However, field tests failed to parallel the greenhouse work, although when the added sulphur was treated with a crude inoculum significantly better uptake was obtained (Mitchell *et al.*, 1952). Apparently, oxidation of the added sulphur was much slower under field conditions than in the greenhouse. Such results

TABLE 2

Effect of Added Sulphur on the Uptake of Phosphorus from Di-calcium Phosphate plus Calcium Nitrate and Mono-ammonium Phosphate in Greenhouse and Field Tests

(*24 lb.* P_2O_5/*acre*)	% S *added*	*Plant weight* (*lb./acre*)	*Uptake of fertilizer* P_2O_5 (*lb./acre*)	% *fertilizer* P *used*
Greenhouse Tests				
Di-calcium phosphate .	0	1,426	2·3	9·6
plus calcium nitrate .	5	1,620	4·8	19·9
Mono-ammonium phosphate . . .	0	1,608	5·0	20·6
L.S.D. (0·05) . .	..	116	0·5	..
*Field Tests**				
Di-calcium phosphate .	0	3,780	1·03	4·3
plus calcium nitrate .	5	4,110	1·03	4·4
	5 (treated)	4,100	1·98	8·3
Mono-ammonium phosphate . . .	0	4,580	5·86	24·4
Check (no fert.) . .	..	3,540	..	..
Check plus S . .	4 lb. S per acre treated	3,550	..	..
L.S.D. (0·05) . .	..	450	0·40	..

* Averages of two tests.

give but another example of the care necessary in interpreting the data of greenhouse experiments and especially in using such data as a guide to field recommendations.

Effect of Placement, Physical State of Fertilizer, and Prevailing Moisture Conditions on Uptake of Phosphorus from the Fertilizer

The common method of fertilizing small grains in this region is by drilling the material so that the fertilizer is placed in the drill row with the seed. The fertilizer used has generally been a granulated mono-ammonium phosphate of 11–48–0 analysis. It appeared desirable to determine the uptake of phosphorus from the fertilizer placed at various depths with respect to the seed, and also to investigate the effect of powdering the granulated material on its availability to the plant. Incidental to the planning of these experiments, it was decided to place two of the three field experiments in a climatically dry part of Saskatchewan in the hope that some indication about the availability of the

fertilizer material under drought conditions might result. The three locations were at Melfort—on a heavy black soil, Kyle—on a heavy brown soil, and at Birsay—on a medium-textured brown soil.

The results of the placement experiments are summarized in Table 3. The data indicate that best results from phosphatic fertilizer applied to wheat or other small grains may be expected when the fertilizer is

TABLE 3

Effect of Depth of Seed and Fertilizer on Wheat Yield
(Average of 3 trials)

(24 lb. P_2O_5 per acre as ammonium phosphate)

Depth of seed and fertilizer	*Grain yield (bu./acre)*	*Total* P *uptake (lb./acre)* P_2O_5	*Fert.* P *uptake (lb./acre)* P_2O_5	*% fert.* P *utilized*	*Fert.* P *as % total in plant*
Seed 3 in. . . .	22·9	15·5	..	..	..
Seed 3 in. Fert. 3 in. .	30·9	18·2	5·7	23·9	31·6
Seed 3 in. Fert. 4·5 in. .	27·7	17·6	5·0	21·0	28·7
Seed 3 in. Trench 4·5 in.	22·6	15·9	..	..	..
Seed 4·5 in. . . .	19·2	13·4	..	..	..
Seed 4·5 in. Fert. 4·5 in.	28·8	17·8	4·7	19·5	26·4
L.S.D. (0·05) . . .	3·5	2·2	0·5	..	..

placed in the drill row with the seed. Although no significant differences in yield appear when the fertilizer is placed below the seed or when both seed and fertilizer are placed at the greater depth of 4·5 in., there is a significantly better uptake of fertilizer phosphate when both seed and fertilizer were placed at 3 in. depth. A decrease in yield resulted in placing the seed at 4·5 in. as compared to 3 in. when no fertilizer was used. For one set of plots (Melfort) the decrease was as much as 10 bu. per acre, a fact which emphasizes the need for care in depth of seeding even in the case of relatively large-seeded crops (Mitchell *et al.*, 1952).

Plots located at Birsay suffered severe and continuous drought throughout the season. The results at Birsay under drought conditions are given in Table 4. The yields are very low, but the fertilizer has resulted in significant increases in yield despite the poor moisture conditions. Perhaps of greater interest is the large percentage of the total phosphorus utilized by the plant that came from the fertilizer. Ordinarily some 20–25 per cent. of the phosphorus in the plant may be derived from the fertilizer (at 24 lb. per acre P_2O_5 as 11–48–0) but under drought conditions over 75 per cent. came from the fertilizer (Michell *et al.*, 1952). This result is contrary to the rather general assumption that phosphatic fertilizers are ineffective in a dry season because of their unavailability to the plant.

In the Birsay test trenching to 4·5 in. and seeding at 3 in. gave a significant increase in yield (Table 4). In neither the Melfort nor Kyle test did this treatment have any effect. It is possible that the effect at Birsay was due to better germination and quicker emergence brought

about through bringing moist soil from the 4·5-in. depth into contact with the seed.

TABLE 4

Effect of Depth of Seed and Fertilizer under severe drought conditions on uptake of soil and fertilizer phosphorus

(24 lb. P_2O_5 per acre as ammonium phosphate)

Depth of seed and fertilizer	*Grain yield (bu./acre)*	*Total* P *uptake (lb./acre)* P_2O_5	*Fert.* P *uptake (lb./acre)* P_2O_5	*% fert.* P *utilized*	*Fert.* P *as % total in plant*
Seed 3 in. . . .	1·41	0·77	..	..	..
Seed 3 in. Fert. 3 in. .	2·98	1·76	1·38	5·9	78·2
Seed 3 in. Fert. 4·5 in. .	2·29	1·23	0·93	3·9	75·6
Seed 3 in. Trench 4·5 in.	3·35	1·52	..	..	..
Seed 4·5 in. . . .	1·41	0·80	..	..	..
Seed 4·5 in. Fert. 4·5 in.	1·76	0·96	0·59	2·5	61·3
L.S.D. (0·05) . .	1·17	0·59	N.S.	..	..

Tests comparing powdered versus granulated ammonium phosphate show little difference in availability as between the two physical states. The results are slightly in favour of the granular condition (Mitchell *et al.*, 1952).

Response of Grain Crops and Varieties of Crops to Phosphates

It is common knowledge that crops differ in the degree of response to phosphates, and this difference in response has been noted in the results of these experiments. Barley and oats respond better than wheat but variations in response may also occur as a result of inherent varietal characteristics (Mitchell *et al.*, 1953).

A tracer test was set out at two locations, one on a less responsive dark brown heavy clay and the other on a highly responsive black moderately heavy soil. Four varieties of wheat (Thatcher, Apex, Redman, and Rescue), three varieties of barley (Titan, Montcalm, and Vantage), and three varieties of oats (Ajax, Exeter, and Fortune) were included in the test. The tests were conducted on fallow land and the fertilizer used was mono-ammonium phosphate at 24 lb. P_2O_5 per acre. Table 5 gives the average response of the two tests in percentage increase over the check, the average uptake of total phosphorus and average uptake of fertilizer phosphorus.

The order of yield increase in these two trials is wheat (least), barley, oats, but it is to be noted that barley utilized a greater proportion of the fertilizer phosphorus and showed a greater uptake of total phosphorus on the fertilized plots.

While, as might be expected, there were a number of significant differences in yield between varieties of the grains attributable to inherent varietal characteristics, it was only in the barleys that differential response to the fertilizer treatment was found. Table 6 gives data in

TABLE 5

Average Increase in Yield and Average Uptake of Total and Fertilizer Phosphorus by Wheat, Barley, and Oats

(24 lb. P_2O_5 per acre as ammonium phosphate)

Grain	*% increase over check*	*Average total P_2O_5 uptake (lb./acre)*	*Average fert. P_2O_5 uptake (lb./acre)*
Wheat . .	34·0	21·1	6·6
Barley . .	39·6	24·4	7·2
Oats . .	54·1	21·7	6·8

TABLE 6

Variety Response to Phosphate Fertilizer by Barleys

(24 lb. P_2O_5 per acre as ammonium phosphate)

Barley variety	*Yield on check plots (bu./acre)*	*Yield on fertilized plots (bu./acre)*	*Increase (bu./acre)*
Titan . .	33·3	53·2	19·9
Montcalm .	54·6	93·0	38·4
Vantage .	46·2	87·2	41·0
L.S.D. (0·05)	..	..	11·4

this connexion. The varieties Montcalm and Vantage gave greater response to the phosphate fertilizer than Titan at Birch Hills, but not at Rosetown on the less responsive soil. Titan is an earlier maturing variety and this factor may be related to the result obtained. Furthermore, this result is only for one test at one location in one season, and would not necessarily represent conditions of response for other soils and other seasons. Nevertheless, it is of interest to observe that such differences between varieties do exist.

Damage from Radiation and the Extent of Adjacent-row Feeding

The matter of possible damage to the plant by radiation from the active phosphorus has always been of concern in such experiments as these. If extensive physiological disturbance to the plant should result from radiation the use of tracer phosphorus in such experiments might be seriously questioned. The direct effect in yield is one test which can be applied to check radiation effects. Disturbance in the uptake of soil or fertilizer phosphorus is also of concern.

Another factor which had to be considered in carrying out field tests with tracer phosphorus was the extent to which the plant might feed on the fertilizer in adjacent rows. In these tests the row spacing has been uniformly kept at 6 in. The general arrangement has been three rows to a plot, with only the centre row being treated with the radioactive fertilizer, this row being harvested for yields and determination of the uptake of soil and fertilizer phosphorus. If the adjacent rows did obtain

some phosphorus from the radioactive row, then a part of the activity would be lost and a distorted result would follow. The adjacent rows were fertilized as were the active rows, but with inactive fertilizer. The fact that adjacent guard rows were present in the tests gave an opportunity to check the extent of adjacent-row feeding and also to check differences in yield that might result from radiation damage.

TABLE 7

Mean Yields of Active and Inactive Rows of Wheat Fertilized with Ammonium Phosphate at 48 lb. P_2O_5 *per acre at Two Locations. Activity at Planting 260 μc.* P^{32} *per gramme* P^{31}

	Birch Hills		*Humboldt*	
	Active rows	*Inactive rows*	*Active rows*	*Inactive rows*
Plant weight, grammes per 6 ft. row at maturity	189·9	189·2	123·2	124·6
% of applied phosphorus utilized . . .	25·0	..	13·6	..

Table 7 gives results comparing yields of adjacent active and inactive rows (Dion Dehm, *et al.*, 1949). As seen in Table 7 there is no significant difference in the weight of plant material as between active and inactive rows with a comparatively large application of the fertilizer and with an activity of 260 μc. P^{32} per gramme P^{31}.

In these experiments the maximum 'piracy' occurring between active fertilized rows and the inactive rows was less than 1 per cent. of the applied phosphorus. It appears that plants have a small tendency to take fertilizer phosphorus from adjacent rows even at only 6 in. distance. The result established that the experimental data are not significantly affected by piracy of the activated phosphorus by plants in the adjacent inactive rows (Dion Bedford, *et al.*, 1949).

Further experiments were designed to determine the effects of various levels of activity on growth and uptake of phosphorus by wheat. In all tests fertilizer was applied as mono-ammonium phosphate at 24 lb. P_2O_5 per acre. The activity ranged from 12 to 3,600 μc. P^{32} per gramme P^{31}.

In greenhouse tests the fertilizer was applied both in solution and in granular form. The plants were harvested after 20, 30, and 40 days' growth.

Where the fertilizer was applied in solution a significant reduction in growth appeared at the 1,200-μc. level of activity at the 20-day harvest and at the 12-μc. level at the 40-day harvest. The latter was accompanied by a significant lowering in uptake of soil phosphorus. In a second experiment where the fertilizer was applied in the granular form at activities of 0, 12, 120, 600, 1,200, and 3,600 μc. P^{32} per gramme P^{31} no alteration in growth or uptake of phosphorus appeared (Penner, 1954 *a*, *b*).

It was considered advisable that further studies on the effects of radiation should be carried out under field conditions. Accordingly field experiments were conducted in the seasons of 1951 and 1952. The

tests were made at two locations, one of which represented the drier Brown or Dark Brown Soils and the other the relatively moist environment of a Thick Black Soil.

The crop used was wheat and the activity levels used in 1951 were 0, 12, 120, 1,200, and 3,600 μc. P^{32} per gramme P^{31}. In 1952 the levels used were 0, 12, 60, 120, 240, and 740 μc. P^{32} per gramme P^{31}. In 1951 the wheat was harvested at three different periods while in 1952 two harvests were taken, one at mid-season and the other at maturity. Criteria used to measure radiation effects were plant weight, total-phosphorus uptake, soil-phosphorus uptake, and fertilizer-phosphorus uptake. In 1951 on the Black Soil statistically significant effects on plant growth appeared at the 12, 1,200, and 3,600-μc. levels of activity at the second harvest only. No deviations appeared at the first or third harvest. On the drier Brown Soil a decrease in plant weight was observed for the third harvest at the 3,600-μc. level while significant deviations occurred in the uptake of fertilizer phosphorus at the 12-μc. level and for both fertilizer and soil phosphorus uptake at the 3,600-μc. level of activity. A significant deviation in soil-phosphorus uptake also occurred at the 1,200-μc. level of activity in the first harvest on this soil. No significant deviations occurred at the second harvest.

In 1952 a significant deviation was observed only once in all the data. It occurred at the mature-harvest date on the Dark Brown Soil where fertilizer-phosphorus uptake was low for the 120-μc. level of activity. In these data deviations attributable to radiation effects are erratic, but appear more likely to occur at levels of activity which are much higher than those generally used in work of the kind reported here (Penner, 1954*a*, *b*).

A careful appraisal of the results obtained in the above experiment leads to the conclusion that deviations due to radiation effects are unlikely to become a source of error in assessing data such as are reported in this paper.

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ISOTOPICALLY EXCHANGEABLE PHOSPHORUS IN SOILS

Part II. FACTORS INFLUENCING THE ESTIMATION OF 'LABILE' PHOSPHORUS

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Summary

Methods used to determine isotopically exchangeable phosphorus in soils are described and briefly analysed. The influence of soil: solution ratio, orthophosphate ions added with radio-phosphorus, the equilibrium pH, and the removal of increasing amounts of phosphate from the soil are investigated. A scheme is suggested for the subdivision of the total soil phosphate into four fractions on the basis of their abilities to exchange PO_4 ions with the phosphate in the soil solution. The relation between the labile pool of soil phosphate and this scheme is discussed.

In an earlier paper (Talibudeen, 1954) a method was described for the determination of isotopically exchangeable phosphate residues in soils, in which 100 ml. of a solution of 0·001 M ammonium citrate and 0·02 M KCl in equilibrium with 0·5 g. of a soil was tagged with a known amount of carrier-free radioactive phosphorus, and the decrease in radioactivity of the solution followed till isotopic equilibrium was attained (in less than 150 hours).

Several other workers have described isotopic-exchange methods to determine the labile 'pool' of phosphate which a crop can utilize. Some of these methods were summarized elsewhere (loc. cit.), and are repeated here together with some more recent work on similar lines. McAuliffe *et al.* (1948) shook 5·0 g. soil in 25 ml. distilled water for 4 days, tagged the solution with 1 ml. carrier-free ^{32}P and determined the radioactivity in solution at various times. They assumed that the readily exchangeable phosphate correlates with the phosphate fertility of the soil and was equal to the fraction for which the distribution of ^{32}P between solid and solution changed logarithmically with respect to time. This change occurs after 20 hours. Wiklander (1950) determined the rate at which labelled phosphate adsorbed on soils exchanged with phosphate ions in solution. He concluded that this exchange was governed by the law of mass action, and that in general the logarithm of the exchange constant approached the equilibrium value of unity logarithmically with respect to time. Gunnarsson and Fredriksson (1953) shook 10 g. soil once daily for 14 days with 1·5 and 3·0 mg. P as labelled phosphate and determined a single value for the labile-phosphorus pool in the soil from the distribution of radioactivity between soil and solution and the total P in solution. This showed remarkable agreement with the phosphate taken up by wheat crops from the soil in pot and field experiments at 3 and 5 rates of superphosphate application respectively. Seatz (1954) shook 1 g. soil with 10 ml. water for 4 days and then added 1 ml. carrier-free ^{32}P. Radioactivity in the solution was measured at various

time intervals up to 7 days, the suspension being shaken intermittently. Here the fractional activity in the solid was plotted against the logarithm of time, and the results (Seatz, fig. 2) suggest that one or two inflexion points, which are assumed to be associated with phosphate fractions of varying abilities to dissociate, occur after 1 hour and 36 hours. It is, however, apparent from these curves that equilibrium or even near-equilibrium is not attained for most soils after 7 days, suggesting the difficulty of calculating an equilibrium value for labile P in the soil. Barbier *et al.* (1954) obtained values of labile P in different soils by tagging their aqueous suspensions with carrier-free ^{32}P, shaking for 24 hours and analysing the solution. They found that for a 120-fold change in soil:solution ratio there was only a 15 per cent. change in the amount of labile P estimated, and that there was good correlation between this value and that obtained from the analysis of leaves and stems of tomato plants in pot experiments. However, they suggest that the discrepancies in their results can be attributed to errors in P estimation, especially with alkaline soils, the lack of attainment of isotopic equilibrium in the stated time, and the preferential attack of root systems on crystalline phosphate residues in the soil. When they added neutral potassium phosphate with the radioactive solution, the time for near-isotopic equilibrium was increased to 5 days. Scott Russell *et al.* (1954) shook 10 g. soil with 200 ml. of a solution containing 5 mg. labelled orthophosphate and determined the ^{31}P and ^{32}P content at various times. From the results for two soils presented, it is clear that isotopic equilibrium is not attained even after 20 days in one case and 50 days in the second. Results have also been given for one soil using four levels of P with measurements at two times; these are dealt with in the Discussion of Experiment 2 in this paper. Experiments by Amer *et al.* (1955) show that for a clay soil and a silt loam, the labile-phosphate pool determined after McAuliffe *et al.* is always larger, more so in the early stages of isotopic exchange, than the phosphate extracted by the Cl form of the strong-base anion-exchange resin Dowex-2. The rate curves for isotopic exchange with the soil and the extraction of phosphate from the soil had the same pattern.

An analysis of the results from these workers suggests that (*a*) at larger soil:solution ratios isotopic equilibrium is attained after much longer times; (*b*) in water suspensions soils of low P status have very low equilibrium-phosphate concentrations in solution, which leads to difficulties in chemical and radiochemical analysis. Moreover, at low soil:solution ratios in aqueous suspension, such systems are unbuffered, causing undesirable pH changes; (*c*) when solutions containing large amounts of tagged phosphate are added to soils, it takes much longer to reach isotopic equilibrium.

The effect of removing increasing quantities of phosphate from a soil on the labile pool and its two components (the soil-surface phosphorus and that extracted into the soil solution) has not hitherto been reported elsewhere.

These considerations have prompted a series of experiments on a few selected Rothamsted soils which are described in this paper.

Experimental

Soils. Data are given in Table 1. The manurial history of the Exhaustion Land soils has been given in detail by Warren (1956).

TABLE 1

Particulars of Soils used

Rothamsted number	*Description*	$CaCO_3$ *content* (%)	*Total* P *content** (*mg.* P/100 *g.*)	*Labile* P *in 0·001 M citrate* (*mg.* P/100 *g.*)	*pH in 0·01 M* $CaCl_2$
A8830 .	Hoosfield Exhaustion Land, arable	2	43·3	4·7	7·5
A8831 .	Ditto	2	59·8	9·4	7·5
A8832 .	Ditto	2	71·6	11·0	7·5
A8867 .	Highfield, pasture	0·1	90·6	17·0	6·7
A8921 .	Sawyer's, arable	0	56·4	9·2	5·2

* Determined by perchloric-acid digestion.

Methods. All experiments were done at 25° ± 0·5° C. with continuous shaking so that the soil was in complete suspension. Tagging with 1–2 μc. of carrier-free ^{32}P was done by adding 0·100 to 0·500 ml. radioactive solution with a micropipette. Unless otherwise stated the amount of labile P in a soil was calculated by dividing the amount of phosphate in solution by the fractional activity left in solution after isotopic exchange for 150 hours.

1. *Soil:solution ratio.* Soil samples varying in weight from 0·5 to 10·0 g. were brought to equilibrium with 100 ml. 0·001 M ammonium citrate in 0·02 M KCl whose pH was adjusted to the pH of the soil in 0·02 M KCl or 0·01 M $CaCl_2$. The solution was then tagged with 2 μc. in 0·1 ml. carrier-free ^{32}P, and the decrease in activity followed with time. Labile-P values at 150 hours are plotted in Fig. 1.

2. *Addition of increasing concentrations of orthophosphate with radiophosphorus.* 0·5 g. soil was brought to equilibrium with 100 ml. 0·001 M ammonium citrate + 0·02 M KCl adjusted to the soil pH as before, and then 25, 125, and 450 γ of tagged P was added in 0·2 ml. of solution with a micropipette. At various times, the solution was sampled for its radioactivity and P content. This experiment was only carried out with one soil, and the results are given in Figs. 2 and 3.

3. *Effect of equilibrium pH on the labile pool.* 0·5 g. of soil was brought to equilibrium with 0·001 M ammonium citrate buffer in 0·02 M KCl whose pH was adjusted to different values with dilute HCl and then tagged with 0·5–1·0 μc. carrier-free ^{32}P. The radioactivity in solution was measured at 150 hours. Labile-P values calculated as usual are plotted in Fig. 4. This was carried out with two soils.

4. *Effect of increasing extraction of soil phosphorus on total labile pool and soil-surface phosphorus.* 0·5 g. soil samples were brought to equilibrium with ammonium-citrate buffers in 0·02 M KCl whose citrate concentration ranged from 0·0001 M to 0·1 M with pH adjusted as in Experiments

1 and 2. The solutions were then tagged with carrier-free ^{32}P and the radioactivity at isotopic equilibrium determined. The 0·0001 M citrate experiment attained equilibrium between 150 and 200 hours whilst the stronger citrate experiments reached equilibrium around 150 hours. Values of the total labile pool and the surface phosphorus were calculated and are given in Table 4.

Results and Discussion

As stated previously (Talibudeen, 1954), the method suggested by the author was designed to fulfil the following conditions: (*a*) The time allowed for attaining isotopic equilibrium covered all the soils used. (*b*) The amount of phosphate in solution even with soils of low P status could be estimated with a standard deviation of ± 2 per cent.; in addition complications due to adsorption of phosphate ions on the walls of the reaction vessel could thus be avoided. (*c*) The use of 0·001 M ammonium-citrate solution to fulfil the latter condition was assumed not to dissolve any solid phosphates in the soil, but only to alter the equilibrium distribution between the micellar phosphate and the phosphate in solution. (*d*) The isotopic-exchange process could be studied under reproducible conditions at chemical equilibrium so that a simple measurement of radioactivity in the solution at different times would give a rate curve due to isotopic-exchange processes.

Experiment 1. Soil:Solution Ratio

Although no systematic study has been made of the influence of the soil:solution ratio on the rate of decrease in radioactivity in the solution, it appears from a few results that, as the soil:solution ratio is increased, the decrease in activity between 100 and 150 hours is considerably greater, and there is an increased lack of equilibrium at 150 hours. An example of the former is given in Table 2 where the decrease in radio-activity of the solution between 100 and 150 hours is expressed as a percentage of the mean activity at those two times.

TABLE 2

Effect of Soil:Solution Ratio on Rate of Decrease of ^{32}P *in solution between 100 and 150 hours*

Soil: Rothamsted No. A8832

Weight of soil per 100 ml. solution	$\frac{(^{32}P)\ 100\ hrs.-(^{32}P)\ 150\ hrs.}{(^{32}P)\ 125\ hrs.} \times 100$
0·5 g.	1
1·0 g.	3·5
2·0 g.	9·2
5·0 g.	17·6

It is clear from Fig. 1 that whereas the labile-P value determined at 150 hours has a constant maximum value at soil weights between 0·5 and 1·0 g., this value falls continuously as the weight of soil is increased. It also appears that isotopic equilibrium is increasingly incomplete at 150 hours as the weight of soil is increased. Thus an equilibrium which

may take some weeks or months to attain in the pot or in the field can be attained in a few days by working at very low soil:solution ratios, i.e. 1:200 to 1:100.

With all the soils examined in this scheme of work isotopic equilibrium is complete within 4–6 days when 0·5 g. soil are used with 100 ml.

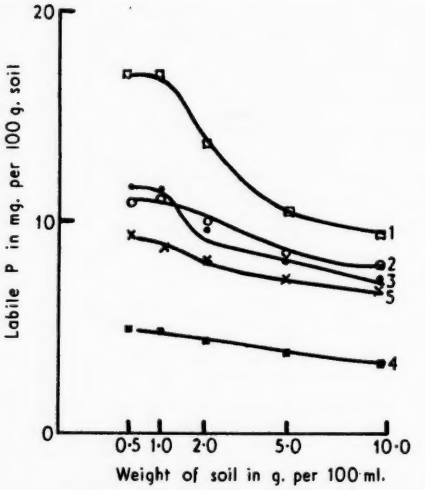


FIG. 1. Labile P and soil:solution ratio after 150 hours exchange. (1) A8867; (2) A8832; (3) A8831; (4) A8830; (5) A8921.

solution, hence the final reading is taken after 150 hours of isotopic exchange.

In contrast to Barbier's finding, these results show a considerably greater decrease in the labile-P pool estimated at 150 hours in these Rothamsted soils (Table 3) with a 20-fold increase in soil:solution ratio.

TABLE 3

Decrease in Labile-P Pool (measured after 150 hours) at Soil:Solution Ratio 1:10 as a Percentage of the Value at Soil:Solution Ratio 1:200

Rothamsted Soil No.	*% decrease*
A8830	46·7
A8831	40·2
A8832	38·6
A8867	43·5
A8921	26·2

However, a direct comparison is not possible because Barbier's values are measured after 24 hours exchange. It will be noticed that this per cent. decrease is around the 40 per cent. level for the neutral and calcareous soils, but drops to 26 per cent. with the acid soil. No general conclusion can, however, be drawn from this single observation.

Experiment 2. Effect of Added Increasing Amounts of Orthophosphate with ^{32}P

Several workers (Gunnarsson and Fredriksson, 1953; Seatz, 1954; Barbier *et al.*, 1954) have attempted to determine the labile pool in soils by addition of orthophosphate ions with the carrier-free radioactive phosphorus and determining the specific activity of the solution at some time when isotopic equilibrium can be assumed to be established with

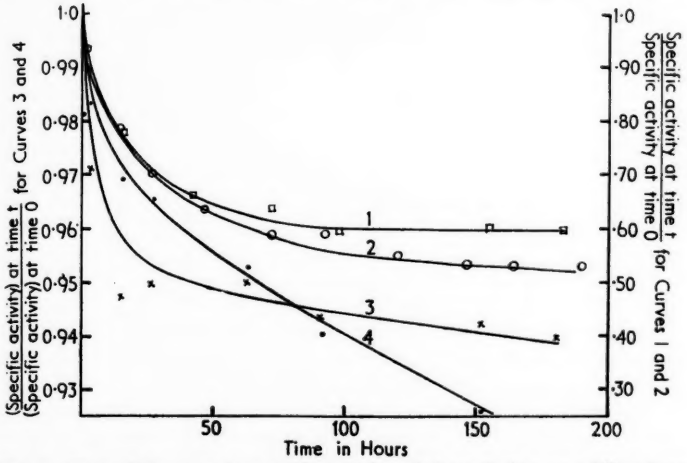


FIG. 2. Rate of decrease in specific activity of the solution on adding four levels of tagged K_2HPO_4 to 0·5 g. soil A8867 in 100 ml. Levels of P added in mg. P per 100 g. soil: (1) 0·02 mg. (carrier free); (2) 5·0 mg; (3) 25·0 mg; (4) 90 mg.

the labile pool of phosphate in soil. In this experiment, a neutral Rothamsted soil containing practically no $CaCO_3$ and a high content of phosphorus resulting from residues of fertilizer application (total P = 90·6 mg. per 100 g.; maximum labile P = 17·0 mg. per 100 g.), was used in order to have a near-ideal system and to see whether in a given time the tagged P would come to equilibrium with the same pool of labile P as when 'carrier-free' ^{32}P was added.

In Fig. 2 the specific activity in the solution is plotted against time. It is quite clear from this that as increasing amounts of P are added with ^{32}P, isotopic equilibrium takes longer to attain. The slope of the specific-activity curve at 150 hours increases as larger amounts of P are added with ^{32}P, whereas at 'carrier-free' levels of added P, isotopic equilibrium is attained before 150 hours and there is no further change in the radioactivity of the solution, i.e. the greater this added P is, the more disturbance is caused to the system. The labile pool in the soil calculated at any arbitrary time will be proportional to the amount of P added, i.e. it will not be a unique value of the soil. This is clear from Fig. 3 where the labile pool in the soil after 150 hours exchange is shown to fall to 70 per cent. of its value with carrier-free ^{32}P on increasing the

added P by 250-fold. The conclusion that, as increasing amounts of tagged orthophosphate are added to the soil, the time required for the attainment of isotopic equilibrium increases seems to be borne out by Barbier's observation (1954, p. 939, and table) that at a soil:solution ratio of 1:100, if 1·94 mg. P_2O_5 is added with ^{32}P, a labile-P_2O_5 value of 344 p.p.m. is obtained after 5 days whereas with the addition of carrier-free ^{32}P a value of 355 p.p.m. is obtained in only 1 day. A result of a

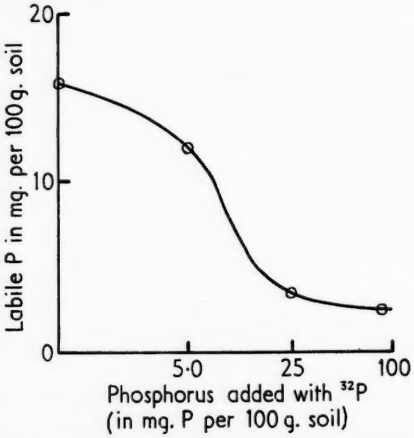


FIG. 3. Labile P in Highfield soil (A8867) after 150 hours exchange.

similar nature is given by Scott Russell *et al.* (1954, p. 94, table 2) where the labile P, estimated by the addition of 2·5–20 mg. P as tagged phosphate in 200 ml. to 10 g. soil, changed the labile P estimated at 4 and 48 hours from 0·61 to 1·69 mg. and 1·49 to 1·77 mg. P per 100 g. respectively. However, the conclusion arrived at by these authors was that 'no significant difference occurred between treatments in the 48-hour sample'.

Experiment 3. Equilibrium pH and the Labile-P Pool

The dependence of the labile-P pool on the pH of the system was studied on a calcareous soil and an acid Rothamsted soil. The results illustrated in Fig. 4 suggest the importance of controlling the pH to the working pH of the soil. Such a study also shows the nature and extent of the alteration of the labile pool if the pH of the soil is changed. For each soil it is seen that the labile pool reaches a maximum with decreasing pH at pH 6·8 for the calcareous soil, and 5·3 for the acid soil. At higher pH values, there is a regular fall in the labile pool in both soils. The import of the pH value of 6·8 for a calcareous soil agrees with the universally accepted idea of the presence of basic calcium-phosphate residues. This evidence suggests that these residues consist of two fractions; the pH-sensitive fraction is completely incorporated into the labile pool as the pH of the system is reduced to 6·8. The remaining

phosphate appears insensitive to a decrease of pH of at least one whole unit from 6·8 to 5·8, hence no further increase is observed in the labile phosphate. The neutralization of an acid soil by the addition of lime or $CaCO_3$, however, is believed to shift the equilibrium from basic aluminium phosphates towards aluminium hydroxide thereby releasing phosphate ions for the use of plants. This experiment in which the pH of the system is raised by the addition of dilute ammonia, whilst keeping

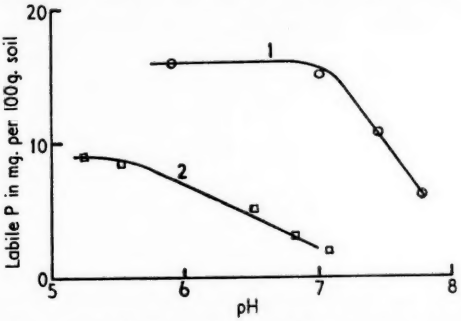


FIG. 4. Labile P and pH. (1) A8832; (2) A8921

a constant concentration of anions other than phosphate, shows a marked decrease in the labile-phosphate pool with increasing pH. This suggests that the increase in phosphate available to plants on liming acid soils is primarily due to an anion-exchange effect whereby high total concentrations of carbonate and bicarbonate ions displace phosphate ions from exchange sites and prevent fixation of added phosphate. An alternative explanation can be based on the commonly accepted theory that on acidifying 1:1 and 1:2 clay minerals, there is a breakdown of the octahedral layers with subsequent migration of partially hydrated Al ions to base-exchange positions. These Al ions may be responsible for tying up labile PO_4 groups which, by 'liming', may be set free by the removal of exchangeable aluminium ions.

Experiment 4. Relation between Phosphate extracted, the 'surface' Phosphate, and the Total Labile Pool of P

In Table 4 the complete analyses of this experiment are given. The 'surface' phosphorus is calculated from the isotope dilution law at isotopic equilibrium

$$\frac{\text{Surface P}}{\text{Surface } {}^{32}\text{P}} = \frac{\text{Solution P}}{\text{Solution } {}^{32}\text{P}}$$

and the total labile P by adding the surface P and the solution P.

The results from all five soils present the same composite picture, which is summarized diagrammatically in Fig. 5. The phosphate extracted by solutions of increasing citrate concentration show a break in extraction curve around the 0·001 M mark. The slope of the extraction curve increases very markedly at concentrations greater than 0·001 M suggesting that there is a change in the nature of the

phosphate extracted beyond that point. Cooke (1940) has reported a similar effect in the extraction of a Kenya lateritic soil (Rothamsted No. A4945) with selenious acid. When 0·5 g. of the soil was shaken up in 200 ml. N/2 acetic acid (the equilibrium pH of the system being adjusted to 2·5 with ammonia), he found that the addition of 0·75–2·5 g.

TABLE 4

The Effect of Citrate Concentration on the Labile Phosphorus Pool, and the 'Surface' Phosphorus in mg. P per 100 g.

Citrate concentration (*M*)	*A8830*		*A8831*		*A8832*		*A8867*		*A8921*	
	Surface P	*Labile* P	*Surface* P	*Labile* P	*Surface* P	*Labile* P	*Surface* P	*Labile* P	*Surface* P	*Labile* P
0·0001	3·9	4·3	6·1	8·6	6·3	10·8	12·7	17·0	0·84	5·7
0·0005	3·7	4·4	5·2	8·5	5·4	10·5	10·6	17·6	3·1	8·8
0·0010	3·4	4·7	5·3	9·4	5·5	11·7	8·3	17·4	4·7	9·2
0·0025	3·5	5·9	6·5	15·2	5·3	14·0	8·1	20·9	6·4	12·1
0·0075	3·6	6·5	6·3	18·6	5·8	21·5	8·7	27·9	5·1	11·9
0·0250	2·9	6·1	6·9	22·2	4·2	21·6	7·6	27·5	6·4	16·7
0·1000	2·8	6·5	6·7	25·9	5·2	34·3	7·7	34·9	5·0	17·3

selenious acid caused little change in the phosphorus extracted. However, increases of 10 per cent. and 100 per cent. on the previous values were observed with 5·0 and 10·0 g. selenious acid, respectively. Fig. 5

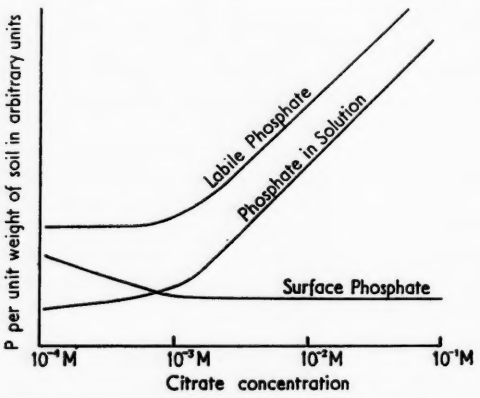


FIG. 5. Diagrammatic representation of Table 4.

shows that the surface-phosphate values descend to a constant value at and beyond this 0·001 M citrate concentration. Thus the total labile-phosphate pool, which is the sum of the phosphate in solution and the surface phosphate remains constant up to the citrate concentration of 0·001 M and thereafter increases in line with the phosphate in solution.

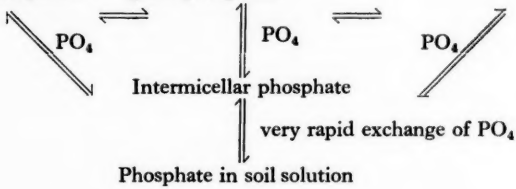
General conclusions

The behaviour of the systems described in this paper can be accounted for by subdividing the total soil phosphate into fractions based on the speed with which they exchange PO_4 groups with orthophosphate ions

in the soil solution. Such a scheme is represented diagrammatically below.

Soil Phosphate Fractions

RAPIDLY EXCHANGING	SLOWLY EXCHANGING	VERY SLOWLY EXCHANGING
Physically sorbed phosphate; phosphate held on external surfaces of minerals and in macro-pores; labile organic phosphate.	Chemi-sorbed PO_4; phosphate held in internal surfaces of minerals and in micro-pores; labile organic phosphate.	Sub-surface solid layers, e.g. apatite crystals; stable organic phosphate.



The pool of labile phosphate referred to earlier includes the phosphate in the soil solution, the intermicellar phosphate, the rapidly and the slowly exchanging phosphate. It is the contention of this paper that this labile pool is measured completely at a dilution of 0·5 g. soil : 100 ml. of a solution whose composition alters only the distribution of PO_4 groups between the soil solution and the rapidly exchanging fractions. The evidence seems to suggest that such a condition is fulfilled for the five Rothamsted soils used here when the solution contains 0·001 M ammonium citrate and 0·02 M KCl.

The influence of the factors investigated on these fractions is significant. The effect of *increasing soil : solution ratios* is to slow down the interchange of PO_4 ions between the phosphate in the internal surfaces and the soil solution. When *tagged phosphate* is added to the suspension, its adsorption and precipitation on the soil matrix slows down isotopic exchange with the labile pool of soil phosphate. The greater the addition, the larger the disturbance produced. Alteration of the *equilibrium pH* changes the balance between the solid phosphate in the soil and the adsorbed and intermicellar phosphate. When this dissolution with decreasing pH stops, no further change in the labile pool occurs. When, however, the extraction is carried out by *increasing concentrations of an extracting agent* which sequesters cations and thereby continuously dissolves the very slowly exchanging solid phase, an interesting situation develops. At very dilute concentrations of the extracting agent, only the balance between the intermicellar phosphate and the phosphate in solution is disturbed. With increasing concentrations, the rapidly and slowly exchanging phosphate is progressively stripped off the soil matrix until only the very slowly exchanging solid-phosphate concentrations remain. The constant surface-phosphorus values determined for all soils at high citrate concentrations then correspond to the surface area of these phosphate concretions.

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THE PHOSPHATE STATUS OF IRISH SOILS WITH PARTICULAR REFERENCE TO FARMING SYSTEMS

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Summary

The phosphorus status of selected permanent pasture and tillage soils has been examined by a fractionation technique. This has shown a distinct difference between the soils especially with regard to the organic-phosphorus fraction. Some of the reasons for these differences are discussed.

The readily available phosphorus level of a highly productive, permanent pasture soil which has received no phosphatic fertilizer for years was found to be good, indicating a satisfactory mineralization of organic phosphorus which was the only form in which this nutrient was added. Irrespective of whether phosphorus was added in the organic or inorganic form there was an appreciable accumulation in the surface 3 in. of permanent pasture, indicating stabilization of applied phosphorus in that zone. Adsorbed phosphorus constituted a relatively small proportion of the inorganic phosphorus, the latter faction varying but slightly in the different soils.

A comparison between Morgan's solution (sodium acetate-acetic acid) and other extractants showed that this solution provides a good index of phosphorus availability, when the P value of the extract is regarded as an intensity value.

When phosphorus fractionation studies were carried out on four soils in hydrologic sequence and occurring in close proximity in an area unmanured for about a century, distinct differences in phosphorus categories were found. These differences were especially striking between the impeded and free-draining members. They were further explored through the medium of fractionation studies on different textural fractions. The main difference was found in the organic-phosphorus level and was associated with the fine-clay fraction.

The general significance of the results in relation to farming systems, the phosphorus cycle and methods designed to determine the phosphorus status of soils, is discussed.

Introduction

Phosphate deficiency is a major chemical problem in Irish soils, the extent of which can be gauged from the fact that in one important dairying area it has been shown (Walsh *et al.*, 1955) that 79·7 per cent. of the grassland soils are very deficient in phosphorus. This same report also shows that on a national scale only 10 per cent. of the soils are adequately supplied with this particular element. While in general farm practice cereal and tillage crops now receive at least moderate phosphate dressings in most districts—either as fertilizer or in farm-yard manure—by far the largest acreage of permanent pasture receives little, if any, phosphatic manures.

Despite this, however, permanent pastures in certain well-known grassland areas in Counties Meath and Westmeath have continued to maintain their quality in terms of herbage type and beef output at a surprisingly good level. While, in general, the system of husbandry practised in those areas—that of grazing relatively mature animals—is rather low in terms of phosphorus exhaustion, chemical tests for readily soluble soil phosphorus show low levels. This has raised the problem of the mechanism whereby the phosphate fertility of these pastures is

maintained. In view of the fact that these soils contain highly satisfactory levels of organic matter (7–9 per cent.) and as organic phosphorus may make a significant contribution to the phosphorus nutrition of plants (Bower, 1945; Rogers *et al.*, 1941) it was considered that a detailed study of this problem might provide a better basis for future developments in the use of phosphatic fertilizers especially on pastures. It is obvious in this connexion that information on the availability of the various phosphorus compounds present in soil, both organic and inorganic, and of the transformations which applied phosphorus undergoes, is highly desirable.

Another problem of a related nature is the extent to which moisture differences in soils influence phosphorus levels. Such differences are very important in farming practice and become especially prominent in high-rainfall areas.

To obtain information on these two points initial investigations were undertaken on the fractionation of phosphorus in some representative soils, and to a lesser extent on the phosphorus status of soils in hydrologic sequence.

Experimental

The phosphorus status of permanent grassland versus mixed arable soils

For this study soils were selected from three distinct areas. These soils are all normally free-draining, representative as far as could be determined of the main management systems in the areas concerned. A brief description of the soils sampled is as follows:

(*a*) *Meath I.* A deep grey-brown loam on glacial drift consisting of limestone and some carboniferous shales, sampled near Dunshaughlin. This soil carries a close herbage mat with *Lolium perenne* and *Trifolium repens* constituting 30–40 per cent. of the sward with *Alopecurus* an important contributor. Fitzgerald (1951) has shown that output to the extent of 3·9 cwt. live-weight gain per acre is obtained on these pastures. This productive soil has received no phosphate fertilizer for many years and is grazed by mature stock for beef production.

(*b*) *Meath II.* A deep grey-brown uniform free-draining loam formed on limestone drift. This soil, though not as productive as the Meath I, carries a rather similar pasture of reputed fattening quality. No phosphate fertilizers have been applied here as far back as available records show.

(*c*) *Louth I.* A uniform free-draining yellow-brown loam on mixed Silurian drift. Frequent attention to phosphatic manuring has been necessary to ensure continued production on this pasture. The soil was obtained at Branganstown (Co. Louth) and has been in pasture for 20 years, the grazing being chiefly by dairy cows and young stock.

(*d*) *Louth II.* This soil was obtained in the same area as Louth I. After a considerable period in indifferent pasture it has been in an arable rotation for 3 years prior to sampling. It received little, if any, fertilizer applications while in pasture.

(*e*) *Wexford I.* A yellow-brown loam on Silurian drift sampled at Cushinstown (Co. Wexford), in a typical tillage area. Soil samples were obtained at the end of a rotation. Frequent attention to phosphatic manuring is essential to ensure good crop yields on these soils. There is evidence of rather rapid phosphate fixation in this area.

Samples were taken from the soils on a profile basis, the sampling depth being determined by profile differences. Some general analyses for these soils are presented in Table 1. The mechanical-analysis determinations were by the International pipette method, while the chemical analyses were by the methods described by Walsh *et al.* (1952). Results for organic matter have been obtained using a modification of Graham's (1950) colorimetric method and total nitrogen by a micro-diffusion technique.

The phosphorus fractionation technique shown in Table 2 is that of Williams (1950) involving successive extraction with 2·5 per cent. acetic acid+1 per cent. 8-hydroxy-quinoline and 0·1 N sodium hydroxide. The ammonium fluoride-hydrochloric acid extraction is that used by Bray (1949). The sodium acetate-acetic acid extractions were carried out according to the modified Peech and English procedure (1944).

The phosphate status of the different soils

The data in Table 2 show considerable differences between the soils under study. For Meath I, it is seen that the phosphorus soluble in 'acetic-quinoline' (which is generally considered to represent the more readily available category and mainly calcium-bound phosphorus) is considerably higher than that present in the less readily available inorganic form. This applies mainly to the surface (0–3 in.), there being a considerable decrease with profile depth. Meath I, because of its much higher level of 'acetic-quinoline'-soluble phosphorus, contrasts sharply with the other soils, especially the rather similar Meath II, and the Wexford I profile which shows such extemely low levels. In the case of the latter soil this difference is in keeping with the lower calcium level and known relatively high activity in phosphate fixation. On the other hand, the Meath II soil has a higher calcium status than Meath I, which suggests that the difference in 'acetic-quinoline' phosphorus fractions of the two soils is indicative of their respective phosphorus-supplying power. While Louth I shows a higher level of this category than Louth II, it is still much below the level obtaining in the Meath I soil, despite a much higher level of phosphate application in recent years. Whether this difference is related to the two different systems of grazing management, i.e. dairying and beef production, remains to be seen.

The inorganic-phosphorus fraction which may be taken as representing mainly the adsorbed and basic iron and aluminium categories, is seen to be at a relatively uniform level for all samples. While in general it is highest in the surface and decreases with profile depth it shows some fluctuations throughout the profile.

Taking extraction with Bray's extractant as a measure of easily acid-

TABLE I

Mechanical and Chemical Analyses for Five Soil Profiles

Soil	Profile depth (in.)	Mechanical anlysis				Chemical analysis						
		Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	pH	Ca (*p.p.m.*)	K (*p.p.m.*)	Org. C (%)	O.M. (%)	N (%)	C/N
Meath I	0–3	15·34	21·07	30·75	17·00	5·7	800	13·5	5·10	8·77	0·36	14·17
	3–7	17·84	25·06	30·50	15·00	5·6	1000	6·0	2·90	4·99	0·19	15·26
	7–14	18·79	25·70	31·75	13·75	5·9	1250	19·0	1·20	2·06	0·09	13·33
	14–18	18·54	17·92	30·75	23·00	6·2	1500	8·5	0·85	1·46	0·11	7·73
	18–23	20·99	16·17	28·75	26·75	6·2	2500	8·5	1·00	1·72	0·13	7·69
	23–33	31·44	17·75	18·75	15·00	6·4	2250	4·5	1·00	1·72	0·12	8·33
	33–36	—	—	—	—	6·3	2250	6·0	—	—	—	—
Meath II	0–3	14·62	25·22	22·50	17·75	5·8	2250	11·0	4·46	7·67	0·35	12·74
	3–7	24·11	26·51	24·50	18·25	6·0	1750	4·5	2·84	4·88	0·20	14·20
	7–15	19·74	27·96	14·50	16·75	6·7	4000	4·5	1·71	2·94	0·16	10·69
	15–24	27·03	21·75	22·25	18·50	7·8	2500	3·0	0·85	1·46	0·06	14·17
	24–30	27·69	22·46	22·00	15·75	7·6	5000	4·5	0·20	0·34	0·05	4·00
	> 30	32·01	15·03	17·50	17·25	7·7	5000	7·5	0·17	0·29	0·05	3·40
Louth I	0–3	29·10	19·25	17·25	20·25	6·0	2000	307	4·24	7·29	0·28	15·14
	3–8	29·32	24·55	20·00	18·25	5·6	1600 −	67	2·50	4·30	0·19	13·16
	8–15	33·35	22·99	20·50	17·25	5·8	2000	12	1·84	3·16	0·15	12·27
	15–26	56·96	20·69	12·50	10·00	6·0	1200 −	17	0·84	1·44	0·05	16·80
	26–35	60·62	17·83	14·00	7·00	6·1	1200 −	12	0·35	0·60	0·03	11·66
	35–38	—	—	—	—	6·0	1200 +	17	0·35	0·60	0·04	8·75
Louth II	0–3	25·49	31·68	23·25	14·70	5·5	1000 −	32	1·89	3·25	0·17	11·11
	3–7	28·69	20·72	23·25	14·75	5·5	1000 −	30	1·89	3·25	0·15	12·60
	7–15	28·14	23·90	20·75	18·00	5·7	800	0	1·17	2·01	0·12	9·75
	15–21	48·04	23·18	17·00	5·00	5·8	400	3	0·50	0·86	0·05	10·00
	21–30	61·80	19·95	10·75	4·25	5·8	400 +	0	0·35	0·60	0·03	11·56
	30–40	69·14	20·26	0·75	2·25	5·8	400	0	0·17	0·29	0·08	2·13
	40–48	61·54	20·56	7·25	5·25	5·7	600 +	0	0·17	0·29	0·04	4·25
Wexford I	0–8	22·48	15·67	23·25	17·75	5·5	200 −	35	2·55	4·39	0·29	8·79
	8–16	23·85	15·67	21·25	20·00	5·8	600 −	11	2·70	4·64	—	—
	16–22	27·19	28·64	23·00	12·50	5·9	400 +	16·5	0·70	1·20	—	—
	22–40	44·43	24·67	22·25	3·00	5·8	800 −	22·5	—	—	—	—

TABLE 2

Phosphorus Fractions in Five Soil Profiles

Soil	Profile depth (in.)	P soluble in 2·5% HAc–8-hydroxy-quinoline (p.p.m.)	P soluble in 0·1 N NaOH				Total P (Pt) (p.p.m.)	P soluble in 0·03 N NH_4F in 0·1 N HCl	P soluble in NaAc–HAc	
			Inorg. P (Pi)		Org. P (Po) Po = Pt − Pi				Single extraction (p.p.m.)	Σ 14 extractions (p.p.m.)
			p.p.m.	% of Pt	(p.p.m.)	% of Pt				
Meath I	0–3	130	45	17·3	215	82·7	260	7·75	5·0	55
	3–7	77	45	23·1	150	76·9	195	5·5	0·25	—
	7–14	30	75	47·8	82	52·2	157	13·0	5·0	—
	14–18	24	33	47·1	37	52·9	70	7·0	0·25	—
	18–23	10	30	85·7	5	14·3	35	1·75	0·25	—
	23–33	34	13	56·5	10	43·5	23	13·0	0·5	—
Meath II	0–3	23	47	29·4	113	70·6	160	3·75	2·0	15
	3–7	33	25	20·8	95	79·2	120	8·75	0·25	—
	7–15	40	25	26·9	68	73·1	93	25·0	5·0	—
	15–24	15	15	33·3	30	66·7	45	5·75	0·25	—
	24–30	23	20	50·0	20	50·0	40	3·0	0·25	—
	30	35	30	100·0	0	0	30	2·5	0·5	—
Louth I	0–3	57	57	23·8	183	76·2	240	19·0	2·25	—
	3–8	15	40	22·9	135	77·1	175	6·5	0·25	—
	8–15	13	35	19·4	145	80·6	180	4·5	0·25	—
	15–26	24	25	50·0	25	50·0	50	13·0	0·25	—
	26–35	20	20	50·0	20	50·0	40	7·5	0·25	—
	35–38	15	15	45·5	18	54·5	33	4·5	0·25	—
Louth II	0–3	33	63	28·3	160	71·7	223	20·5	2·25	30
	3–7	40	25	12·3	178	87·7	203	21·0	1·5	—
	7–15	15	25	15·2	140	84·8	165	4·0	0·25	—
	15–21	20	15	37·5	25	62·5	40	14·5	0·25	—
	21–30	15	15	37·5	25	62·5	40	10·5	0·25	—
	30–14	63	35	100·0	0	0	35	19·5	0·25	—
Wexford I	0–8	3	55	47·9	60	52·1	115	5·5	1·0	9·5
	8–16	10	41	27·9	106	72·1	147	5·75	0·25	—
	16–22	10	22	31·9	47	68·1	69	4·25	0·25	—
	22–40	—	—	—	—	—	—	5·5	0·25	—

soluble phosphorus as well as adsorbed phosphorus, it is apparent that this represents, with some exceptions, but a relatively small part of the inorganic-phosphorus category. This is particularly so in the case of Meath I, Meath II, and Wexford I. The Louth I and Louth II samples —especially the latter—show the highest levels of this category, these soils also having received the most attention through phosphatic manuring. Under the conditions of pH and base status existing it is reasonable to expect that there should be a build up in this category.

The organic phosphorus shows a distinct difference between the different soils especially considering the management and cropping history. Meath I has a much higher content of this fraction and contrasts sharply with the tillage soil Wexford I. While the two tillage soils show little difference in organic-phosphorus content between the surface and the subsurface samples, there is a well-defined and sharp decrease with depth for the pasture soils. This implies that the main location of this category in pasture soils is in the surface, irrespective of whether the main return is in the organic form through the animal (i.e. for Meath I and Meath II) or through fertilizer and animal (i.e. for Louth I). Taking the figures shown, in relation to the organic matter and nitrogen levels in the soil, it can be seen that while for each individual soil there is a parallel between organic matter and organic phosphorus, the relationship between different soils is not so straightforward. This is particularly so for the two Meath soils which although having approximately the same organic-matter content show a big difference in organic-phosphorus status. This effect is even more prominent for the Louth soils which, while showing a big difference in organic matter, do not differ very appreciably in organic-phosphorus content. These differences are illustrated in Fig. 1.

It is seen from Table 2 that Morgan's sodium acetate-acetic acid solution, as compared with the other extractants used, removed very small quantities of phosphorus in one extraction. This is the normal extraction procedure used in this Laboratory. Morgan (1941), however, pointed out that the amounts extracted in a single extraction represented but a small—though proportional—amount of the readily soluble category. On this basis, the quantity soluble in this extractant may be regarded in the same light as a neutral salt solution and as an index of phosphorus solubility rather than representing a specific category of soluble phosphorus. The quantity present in solution will be, as with a neutral salt solution, the end product of a number of reactions between soil and solution. Such factors as negative adsorption in relation to the sodium ion and soil type, and the formation of iron and aluminium complexes in relation to length of extraction time and phosphorus re-adsorption, are of obvious importance.

The data in Table 2 do, however, reflect phosphorus-supplying power when related to the fertility status of the soils under study. This is made abundantly clear in the data for fourteen successive extractions of four of the surface soils (Fig. 2). This figure shows phosphorus in solution at each extraction plotted against the number of extractions. It is evident that Meath I shows a clear-cut difference from Meath II,

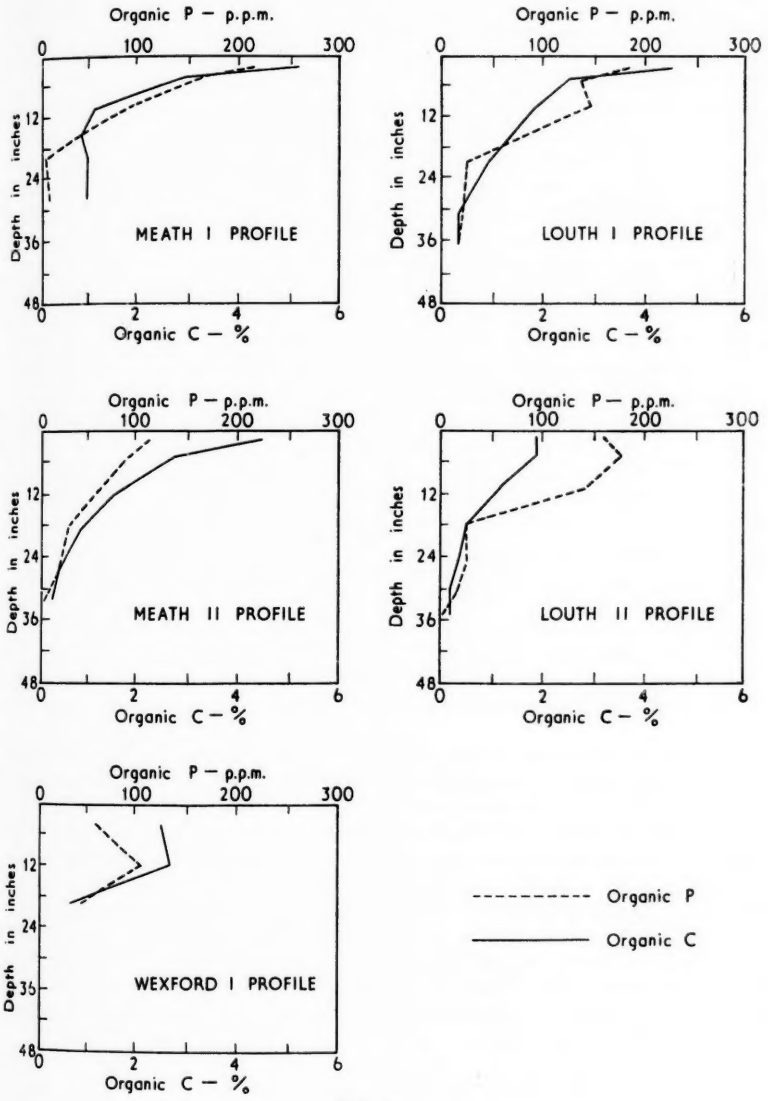
Organic P — p.p.m.
0
100
200
300
Depth in inches
12
24
36
48
MEATH I PROFILE
0
2
4
6
Organic C — %
Organic P — p.p.m.
0
100
200
300
Depth in inches
12
24
36
48
LOUTH I PROFILE
0
2
4
6
Organic C — %
Organic P — p.p.m.
0
100
200
300
Depth in inches
12
24
36
48
MEATH II PROFILE
0
2
4
6
Organic C — %
Organic P — p.p.m.
0
100
200
300
Depth in inches
12
24
36
48
LOUTH II PROFILE
0
2
4
6
Organic C — %
Organic P — p.p.m.
0
100
200
300
Depth in inches
12
24
36
48
WEXFORD I PROFILE
0
2
4
6
Organic C — %
Organic P
Organic C

FIG. 1.

Louth I and Wexford I—supplying almost six times as much readily soluble phosphorus as the latter soil. The conclusion therefore is that extraction with Morgan's solution provides an index of phosphorus-supplying power and ability to maintain a supply of phosphorus to the soil solution.

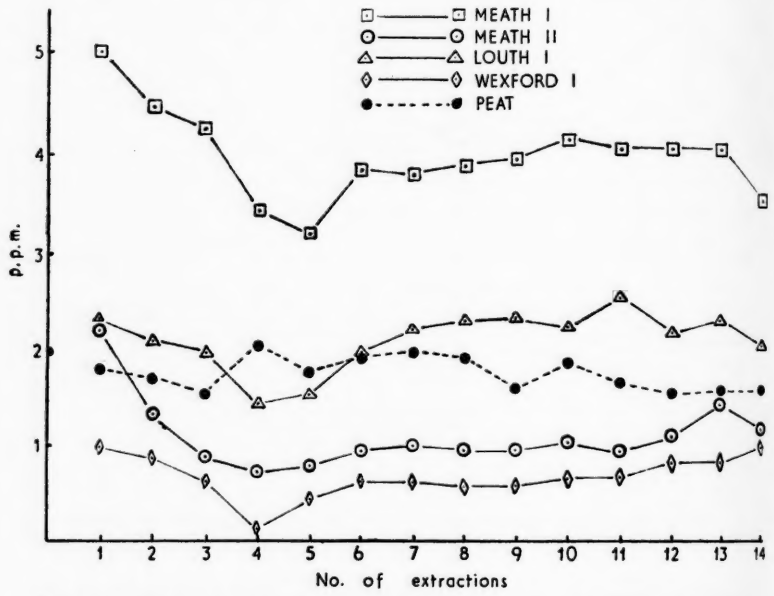

FIG. 2. Phosphorous release on successive extraction with Morgan's solution.

In most instances it is seen that following a slight initial fall in the quantity of phosphorus extracted, successive extracts show little variation in phosphorus content up to the fourteenth extraction applied. The peat sample included is from a soil showing a very phosphate-deficient condition as measured in crop response to fertilizer application. In interpreting the significance of acetic acid-sodium acetate phosphorus data, it is the experience that highly organic soils present a very different problem from mineral soils, in that very deficient organic soils show considerably higher phosphorus values than similarly phosphate-responsive mineral soils. This, from the information at present available, seems to be related to the re-adsorbing action of aluminium and iron complexes in mineral soils.

Phosphorus fractions as related to moisture variations

Under normal farming conditions differences in drainage—as reflected in gleying at various depths—are of considerable practical importance in relation to fertilizer use. In studies of a hydrologic sequence Glentworth (1947) has shown that there are distinct differences

in phosphate status between free-draining and impeded members. Walsh *et al.* (1950) found that for the extremes of this sequence, i.e. the free-draining and strongly impeded, a significant difference occurred only between surface samples, which showed a retention with Brays extractant, of 72 and 41 per cent. respectively.

In order to get more information on the phosphorus status of the varieties in hydrologic sequence, it was considered that fractionation studies might be of interest. The soils selected occur in close association on a common parent material of mixed drift comprised of Cambrian-Silurian shales and quartzites. The profiles were similar to those previously examined (Walsh *et al.*, 1950), the free-draining strongly leached acid brown loam being situated some 150 yds. distant in the same field from the impeded, the two intermediate categories being situated in between. The field has had no manurial treatment for at least a century, being grazed for portion of that time by deer. The vegetation consists of *Agrostis* spp., *Festuca* spp., and some *Pteris Aquilina* in the free-draining; the impeded variety carrying mainly a carex-juncus community.

Data for the mechanical and chemical composition of the four soils studied are presented in Table 3, while the results from the phosphorus fractionation are presented in Table 4.

While it is clear that the phosphorus in each category is at a low level as compared with (say) Meath I, a definite difference exists between the different varieties for the organic phosphorus category. It is seen that in the surface 6 in. depth there is a definite decrease in this particular phosphorus category from 75 p.p.m. in the free-draining to 40 p.p.m. in the strongly impeded variety. An especially notable feature is the sharp decrease with the profile depth in the case of the latter, a more gently graded decrease showing for the other varieties. It is also apparent that at a depth of 18–24 in. the free-draining member has a similar quantity of phosphorus in the organic category as the surface soil of the strongly impeded.

The evidence available from this study does not entirely support the findings of Glentworth (1947) regarding the occurrence of a high proportion of readily soluble phosphorus in the G horizon which in the case of profile B (slightly impeded) begins at 18 in., profile C (moderately impeded) at 12 in. and profile D (strongly impeded) at approximately 4 in. The significance of the comparison between the two methods is, however, doubtful, as Glentworth's results refer to straight acetic acid extraction at pH 2·6 while the present results were obtained with acetic acid plus the blocking agent 8-hydroxy-quinoline. It is also possible that the effect reported by Glentworth, who was dealing with soils under ordinary agricultural treatment, may be a function of applied phosphorus.

Regarding the 'acetic-quinoline' and inorganic categories, it is of interest that while the impeded variety has a higher base status than the free-draining, this is not accompanied by an increase in calcium-bound phosphorus. It has previously been shown (Walsh *et al.*, 1950) that there is a much higher level of easily soluble aluminium in the surface soil of the free-draining variety. This is to a slight extent reflected in a higher level of inorganic phosphorus.

TABLE 3

Mechanical and Chemical Analyses of Hydrologic Series

Soil	*Profile depth (in.)*	*Mechanical analysis*				*Chemical analysis*			
		Coarse sand (%)	*Fine sand* (%)	*Silt* (%)	*Clay* (%)	pH	Ca (*p.p.m.*)	K (*p.p.m.*)	*Organic matter* (%)
Profile A: Free-draining	0–6	21·5	25·9	18·75	14·75	4·9	200	98·0	5·16
	6–13	19·5	32·0	20·3	18·5	4·9	200	19·5	3·25
	13–19	24·7	31·6	19·5	16·25	4·9	200	8·5	2·60
	19–24	25·2	28·9	19·0	17·0	4·9	200	3·0	1·72
	> 24	23·0	33·5	20·8	16·25	5·3	200	6·0	1·40
Profile B: Slightly impeded	0–6	22·26	29·2	19·0	17·0	4·9	200	92·0	5·90
	6–12	29·78	26·2	19·3	18·25	5·1	200	53·0	2·60
	12–18	26·5	17·7	22·5	27·25	5·3	400	19·5	1·11
	18–24	55·05	17·5	10·3	13·75	5·5	400	13·5	0·30
	> 24	44·2	15·4	16·8	21·0	5·5	400	19·0	0·30
Profile C: Moderately impeded	0–6	17·98	34·2	20·8	14·0	5·3	200	25·0	4·55
	6–12	21·0	31·8	21·0	18·0	5·6	600	25·0	2·05
	12–18	14·43	31·6	26·0	22·25	5·8	1000	19·5	1·11
	18–24	10·35	29·5	25·5	28·75	6·0	1000	11·0	0·73
	> 24	17·54	27·8	23·8	26·0	6·0	1000	13·5	0·60
Profile D: Strongly impeded	0–6	22·75	31·9	18·0	10·75	5·5	600	22·5	4·55
	6–12	31·1	32·0	15·3	11·50	5·8	600	13·5	2·35
	12–18	23·25	27·6	24·3	20·25	6·0	800	11·0	1·11

TABLE 4

Phosphorus Fractions in a Hydrologic Profile Series

Soil	*Profile depth* (*in.*)	P *soluble in* 2·5% HAc—*8-hydroxy-quinoline* (*p.p.m.*)	P *soluble in* 0·1 N NaOH				*Total* P (Pt) (*p.p.m.*)	P *soluble in* 0·03 N NH_4F *in* 0·1 N HCl (*p.p.m.*)	P *soluble in* NaAc—HAc *Single extraction* (*p.p.m.*)
			Inorg. P (Pi)		*Org.* P (Po) Po = Pt—Pi				
			p.p.m.	% *of* Pt	*p.p.m.*	% *of* Pt			
Profile A: Free-draining	0–6	20	23	23·5	75	76·5	98	6·5	0·50
	6–13	13	15	18·1	68	81·9	83	3·0	0·25
	13–19	13	15	20·0	60	80·0	75	2·0	0·25
	19–24	10	15	27·3	40	72·7	55	2·5	0·25
	> 24	13	13	37·1	22	62·9	35	3·8	0·25
Profile B: Slightly impeded	0–6	20	23	27·7	60	72·3	83	—	0·25
	6–12	25	20	29·4	48	70·6	68	—	0·25
	12–18	13	15	45·4	18	54·6	33	—	0·25
	18–24	13	15	45·5	18	54·6	33	—	0·25
	> 24	15	13	56·5	8	43·5	23	—	0·25
Profile C: Moderately impeded	0–6	20	20	30·8	45	69·2	65	—	0·25
	6–12	15	13	27·7	84	72·3	47	—	0·25
	12–18	13	15	50·0	15	50·0	30	—	0·25
	18–24	13	13	26·5	10	43·5	23	—	0·25
	> 24	10	20	100·0	0	0	20	—	0·25
Profile D: Strongly impeded	0–6	15	15	27·3	40	72·7	55	8·5	0·25
	6–12	10	10	43·5	13	56·5	23	4·2	0·25
	12–18	7	3	20·0	12	80·0	15	0·5	0·25

Phosphorus status of the clay and fine-sand fractions

As may be seen from Table 3 these soils are relatively uniform with regard to textural composition, and surface organic matter content, while in addition, cultural treatment has been uniform. The only variable—apart from vegetation—has been moisture differences. As Williams[1] has found the phosphorus content of different textural grades a valuable index of phosphorus status, it was considered that a further fractionation on a textural basis might be of interest, in view of the differences reported in Table 4. For this purpose the clay and fine-sand fractions of the two drainage extremes—the free-draining and impeded varieties—were selected for further study. The clay fraction ($< 0{\cdot}001$ mm.) was obtained by dispersion for 30 min. with a Waring-Blender using CO_2-free distilled water followed by decantation. Concentration of the suspension was carried out on a water-bath and subsequently dried over silica gel. The fine-sand fraction (0·2–0·02 mm.) was obtained by the appropriate settling and decantation technique. In order to ensure a strong extraction of the fine-sand fraction and the breakdown of mineral phosphate the relatively rigorous extraction technique of Mehta *et al.* (1954) was employed. This procedure involves successive extractions with concentrated HCl and 0·5 N NaOH with a final extraction with 0·5 N NaOH at 90° C. The technique was applied to the two mechanical fractions (i.e. clay and fine-sand fractions) and the whole soil. The results for this fractionation are presented in Table 5.

From Table 5 it is seen that this technique has extracted much more phosphorus in the different categories than the Williams (1950) technique. In view of the more vigorous extraction this is to be expected. Very much higher figures by the Mehta extractants are shown for both inorganic and organic phosphorus, especially where the former is concerned, indicating a greater degree of attack on the inorganic complex. The figures also show quite clearly that a considerable proportion of the phosphorus present in the organic form is in a relatively stable condition, dephosphorylating only with difficulty. Extraction by the Mehta technique does not, however, give as clear a picture of the more readily available phosphorus as does the Williams technique, the phosphorus status of the soil being extremely low.

Phosphorus in both the inorganic and organic forms appears to be predominantly located in the clay fraction, there being a considerable difference between the quantities associated with the clay from the free-draining and impeded varieties. The most striking difference in this connexion is for the organic fraction. This is especially significant as the organic-matter content of the clay fraction of both varieties is approximately equal. As might be expected, the phosphorus in the fine-sand fraction is mainly in the inorganic category, the total level, however, being low—indicating little reserve in the way of weatherable minerals. This shows clearly also that the main transformations in the phosphorus cycle in this soil where a high degree of equilibrium has

[1] Private communication.

TABLE 5

Phosphorus Distribution in the Clay and Fine-Sand Fractions of a Free-draining and Impeded Profile by the Mehta Technique

Soil	Profile depth (in.)	*Inorg.* P (Pi)			*Org.* P (Po) (Po = Pt−Pi)			*Total* P (Pt)			Organic matter in clay fraction (%)
		Soil (p.p.m.)	Clay (p.p.m.)	Fine sand (p.p.m.)	Soil (p.p.m.)	Clay (p.p.m.)	Fine sand (p.p.m.)	Soil (p.p.m.)	Clay (p.p.m.)	Fine sand (p.p.m.)	
Profile A: Free-draining	0–6	212	679	69	330	1,654	15	542	2,330	84	15·65
	6–13	131	525	56	264	1,308	29	395	1,830	84	7·60
	13–19	136	612	69	272	1,263	35	408	1,875	104	6·95
	19–24	162	400	86	119	475	39	281	875	125	2·60
	> 24	200	325	86	50	258	23	250	580	104	2·35
Profile D: Strongly impeded	0–6	156	375	62	198	466	42	354	878	104	15·14
	6–12	118	312	56	132	604	6	250	916	62	9·65
	12–18	118	225	62	46	233	0	166	458	62	3·15

been reached with environmental conditions are between the highly weathered clay material and its associated organic matter.

While both the Williams and Mehta fractionations show a sharp decrease in total soil phosphorus in the 6–12 in. depth of the impeded variety, it is seen that the clay-fraction organic phosphorus shows a very substantial rise. The reason for this occurrence is not at present obvious.

Some general considerations

It has been shown that once a proper basis for interpretation is arrived at, the importance of which in phosphate availability studies is particularly stressed by E. G. Williams (1952), the different methods used furnish a good picture of the phosphorus fertility status. For instance, while 'acetic-quinoline' phosphorus is more an absolute measurement, acetic acid-sodium acetate soluble phosphorus is more an index of continual-release phosphorus. In the light of the data provided by the fractionation techniques employed in this study, it has been possible to account for the productive capacity of some old pasture soils in the absence of any applied fertilizer phosphorus.

Although one of the soils studied (Meath I) has a relatively satisfactory supply of phosphorus, another soil (Meath II) which is more representative of the soils in the area has a phosphorus level approaching the critical point below which deterioration may occur. Such deterioration could obviously be hastened by the introduction of a more demanding type of husbandry such as dairying or the raising of young stock. The probable effect of such a change is understandable from a consideration of the phosphorus status of the Louth I soil, which, although receiving generous applications of phosphate in fertilizers, shows a considerably lower all-round phosphorus status by comparison with Meath I. The differences as shown by fractionation are mainly reflected in the calcium-bound and organic phosphorus categories. This is reasonable in view of the close association between these two categories in phosphorus-cycle transformations, under the influence of seasonal biological changes. Furthermore, these differences are mainly located in the surface layers, the implication being that under pasture conditions phosphorus accumulation can be effected either in applications of phosphatic fertilizer or through the organic cycle in the animal.

However, as a rigid separation into individual categories is not possible due to the dynamic nature of the phosphorus cycle as discussed by Pierre (1948), an understanding of the transformations within the cycle and the soil factors affecting it is important. Pertaining to this, the mineralization of organic matter and the accompanying changes in phosphorus status are of special significance. Directly involved in these transformations are such factors as the relative organic-matter and nitrogen contents; the nature of transformation products in terms of organic acids and salts; the relative rates of CO_2 evolution; the level of active sesquioxide material present and the nature of the clay minerals, especially from the aspect of differential adsorption of specific organic fractions. In view of the high production particularly from the Meath I soil, it is evident that in this particular instance, at least, optimum or

near optimum conditions obtain with regard to the factors mentioned above for the mineralization of the organic phosphorus compounds.

The part played by moisture is well shown by the fractionation study of soils in the hydrologic sequence where it has been possible to study long-term effects under natural conditions. While the free-draining soil, after a century, now shows a much more satisfactory phosphorus status there is no simple explanation to hand. The difference is one solely of organic phosphorus. Possibly this difference is the consequence of a higher phosphorus level in herbage developed under conditions of free-drainage, or even the presence of a specifically resistant type of organic phosphorus complex in the herbage. Again, the higher level of active sesquioxide material in the free-draining soil may have had a stabilizing influence through the formation of iron and aluminium salts with organic phosphorus complexes, resulting in a similar effect as, for instance, when phytin is added to acid soils (Bower, 1945). The free-draining soil has been shown (Walsh *et al.*, 1950) to contain a higher level of active iron and aluminium than the impeded variety. The main centre of activity in these particular soils is seen from the textural fractionation study to be located in the highly weathered clay-humus fraction.

Although the fractionation study has shown, with some exceptions, a direct relationship between organic phosphorus, organic carbon, and nitrogen, there is evidence that increased mineralization results in a lowering of the C/P ratio, thus paralleling the C/N ratio. While this is particularly well shown by the Louth II soil, which has a lower organic C and N content than Louth I but has approximately the same organic P content, it must be also borne in mind that possible variations in the degree of completeness of extraction of the total organic P in the different soils might be a complicating factor, particularly with the use of the Williams technique. However, there is little likelihood of such variations occurring in the case of the hydrologic series studied using the Mehta technique for reasons already outlined. The occurrence of rather stable specific organic-matter complexes in intimate association with the highly weathered clay fraction is implied.

Finally the analytical data presented in this study should provide a better understanding of the factors influencing the phosphate fertility of some Irish soils in relation to different farming systems.

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THE REACTION BETWEEN PHOSPHATE AND PHOSPHATE-FIXING SOILS

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Summary

Phosphate-fixing soils and hydrated iron and aluminium oxides have their power of sorbing phosphate reduced if they are pretreated with reagents forming insoluble or unionized compounds with iron and aluminium ions. Soils sorb many more milliequivalents of these blocking reagents than correspond to the drop in their phosphate-sorbing power, and it does not seem to be possible for a soil to sorb so much of one of these reagents that it ceases to sorb phosphate. Blocking reagents such as potassium ferrocyanide and 8-hydroxy-quinoline cannot be used to distinguish hydrated iron from aluminium oxides as the agents causing this phosphate sorption.

Soils which have been treated with hydrosulphite to remove some of the free hydrated iron and aluminium oxides still sorb phosphate, but this sorption is reduced to a very low value if the soil is then treated with a blocking reagent. The fulvic acid fraction of soil organic matter is a good blocking agent. Fulvic acid and blocking reagents such as aluminon and alizarin S cause the soils to deflocculate in 0·1 N sodium acetate.

Introduction

THE object of this work was an investigation of the possibilities of 'blocking' soils as a basis for measuring quantitatively the relative importance of hydrated iron and hydrated aluminium oxides in the sorption of phosphate by acid soils known either to be well supplied with the free oxides or else to fix phosphate in forms unavailable to agricultural crops. The method adopted was to study the effect of pretreating the soil with reagents which form insoluble compounds or stable chelates with ferric ions or with ferric and aluminium ions, and was therefore a development of a method first used by Ghani (1943) and extended by Williams (1950) and Cooke (1951). Ghani showed that N/2 acetic acid containing 5 per cent. 8-hydroxy-quinoline (oxine) dissolved more phosphate out of Indian soils than the acetic acid by itself, and this difference was greatest for soils in the pH range 4–5 and was negligible in neutral soils.

Ghani interpreted this result as showing that iron or aluminium hydroxides in the soil were reabsorbing phosphate dissolved out of the soil by the acetic acid, and that the oxine prevented, or at least reduced, this reabsorption. Cooke extended this work by comparing the effect of reagents other than oxine in the acetic acid, and concluded that a N/2 acetic acid solution containing 0·5 per cent. selenious acid effectively prevented hydrated iron and aluminium oxides from sorbing phosphate from the acid solution, though the effect of the selenious acid was not so marked if a lateritic soil was used instead of the pure hydroxides. Both Cooke and Williams used solutions which were about 0·07 M in oxine or selenious acid and 10^{-4}–10^{-5} M in P, so that the blocking agent was 100–1,000 times more concentrated than the phosphate. Cooke adjusted the pH of his solutions to 2·5.

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Materials Used

1. *Soils and clays*

Three soils were used in this work.

Soil A. A tropical red earth (latosol) from a sisal estate near Ngomeni, Tanganyika. It is a subsoil from 18–26 in. deep, red-brown in colour, derived from a biotite gneiss, pH (water) 5·9, and containing 16 m.e. exchangeable cations (determined from retention of barium from a 1 N $BaCl_2$ solution.) Appreciable quantities of goethite and perhaps some haematite were present.

Soil B. A medium loam from Drakemyra Farm, Grantshouse, Berwickshire (Scotland), derived from Silurian and Old Red Sandstone drift. It was chosen as an example of a 'phosphate-fixing' soil, that is the land is well farmed and well manured, yet the 'available phosphate' remains in the trace category. Its pH (water) is 6·0 and it contains 45 m.e. exchangeable cations. Dilute acid leachates contain appreciable amounts of aluminium but no iron. Soil B was given to us by A. M. Smith of the Edinburgh and East Scotland Agricultural College.

Soil C. A loam from Greenhall Farm, Aberdeen, derived from gabbro, and showing 'phosphate-fixation' even more strongly than soil B. Its pH is 5·8, and it contains 12 m.e. exchangeable cations, and dilute acid leachates contain appreciable amounts of iron but little aluminium. This soil was given to us by E. G. Williams of the Macaulay Institute for Soil Research, and is similar in behaviour to that used by him (Williams, 1950).

Soil D. A few experiments with this soil, made by B. W. Bache of this laboratory, are reported here. The soil is a clay loam from Larne, Antrim, N. Ireland, derived from basalt. Its pH (water) is 5·5, it has 34·5 m.e. exchangeable cations, 7·2 per cent. organic carbon. This soil contained 2–3 per cent. haematite and some amorphous sesquioxides, mostly of iron. It was given to us by S. M. McConaghy of Queen's University, Belfast.

In addition a few experiments were made with some clays, namely a commercial sample of Wyoming bentonite, a St. Austell kaolin, and a metahalloysite from Bedford, Missouri. A. Newman, who gave us this last sample, checked its purity by X-ray, but he obtained evidence from dielectric-loss measurements that it may have contained a little hydrated alumina.

2. *Hydrated iron and aluminium oxides*

Goethite. This was prepared in two ways. Goethite (1) was made by hydrolysing ferric chloride with ammonia, and ageing the brown gel so formed by boiling for 19 hours (H. B. Weiser, 1935). It was then dried under vacuum and was a red powder. X-ray photographs gave good goethite lines, and none other, and D.T.A. indicated it contained 75 per cent. goethite. This preparation was meant to be haematite, but in spite of its colour, it contained none. Goethite (2) was made by bubbling air through a dilute solution of ferrous sulphate and sodium carbonate, and drying as before (J. J. Fripiat and M. C. Gastuche, 1952). It was a red-brown powder, more poorly crystalline than goethite (1) and

contained an appreciable proportion of cold precipitated iron oxide. A number of samples of each of these goethites were made and their phosphate-sorbing power measured, and it was found that every factor giving better crystallization or greater dehydration reduced the phosphate-sorbing powers, as one would expect.

Cold precipitated iron oxide. This was recognized and named by Mackenzie (1952), and is the unaged but dried-down brown gel initially produced when goethite (1) is being prepared.

Lepidocrocite was made by van Schuylenborgh and Sänger's method (1949). Sodium thiosulphate was added to a solution of ferrous sulphate and ammonium chloride, and the ferrous iron oxidized with potassium iodate at 45° C. It was a fluffy orange powder, which appeared to be almost pure lepidocrocite.

Bayerite was made by precipitating aluminium hydroxide from aluminium sulphate by adding sodium hydroxide and washed free from sulphate. This was then dissolved in the minimum amount of dilute NaOH, and the bayerite precipitated by bubbling air through it.

Boehmite was prepared by adding ammonia to aluminium chloride and ageing the precipitate by boiling for 3 hours. The purity of these hydrated aluminas was checked by X-ray and D.T.A. All this X-ray and D.T.A. work was kindly done for us by D. J. Greenland and R. C. Mackenzie.

3. *Fulvic acid*

This was prepared from an old neutral pasture soil, by treating it with a 2:1 mixture $NaHCO_3$:Na_2CO_3, pH 9·1, which was 0·4 N in carbonate, at 55–60° C. for a few hours. The extract was run through a Sharples super-centrifuge to remove as much clay as possible, and then converted to the free acid by treating with the hydrogen form of Amberlite IR 120 resin. The humic acid was removed by flocculating with 0·2 N H_2SO_4 and centrifuging. The fulvic acid was then freed of sulphate by passage through a column of the hydroxyl form of Amberlite IR 400 resin. The fulvic acid fraction was used in preference to the total organic extract because it remains dispersed in the sodium-acetate buffers added to the soil in phosphate-sorption experiments.

Experimental Methods

The conditions under which the soils sorbed phosphate were standardized as far as possible. In a typical experiment 1 g. soil was put in a Pyrex boiling tube and shaken up with three successive lots of 40 ml. of 0·1 N sodium acetate buffered either to pH 5·5 or pH 3·5. It was then shaken with a further lot of acetate, to which had been added 1 mg. P as NaH_2PO_4 and two drops of toluene to reduce microbial activity The tubes were put on an end-over-end shaker and after selected times, usually 2·4, 24, and 240 hours, taken off and 1 ml. of fairly clear solution was pipetted out, put into 5 ml. of 1 N NaCl, cleared by centrifuging, and the phosphate determined on an aliquot by Zinzadze's (1935) method. When the pH 3·5 buffer was used, sufficient NaCl was added to bring the ionic strength up to 0·085 unit, which was that of pH 5·5 buffer.

The only uncontrolled factor affecting phosphate sorption was the variation in laboratory temperature, which probably caused an extreme variation of 10–15 per cent. throughout the year, but for comparisons made at about the same time this error is believed to be small. Each result reported is the mean of determinations from three tubes, and the standard error of this result, which is about 0·015 mg. P, includes errors due to variations in laboratory temperatures over reasonable periods of time.

Preliminary Experiments mainly with Soil A (Tanganyika subsoil)

Unless specifically stated, 1 g. untreated soil was shaken with 40 ml. 0·1 N sodium acetate at pH 5·5 containing 1 mg. P.

1. *The effect of time of shaking and quantity of* P *added*

Provided a reasonable amount of P remained in solution, the rate of sorption of P decreased linearly with the logarithms of the time of shaking over the range 10 min. to 240 hours. By varying the amount of soil and of P added, four final concentrations of P in solution were obtained, ranging from 0·23 to 14·3 mg. after 96 hours. The relation between the amount of P sorbed per gramme soil and the concentration of P left in solution followed the Langmuir equation. Further, if the soils which had sorbed phosphate were then shaken with the phosphate-free buffer, the amount of phosphate desorbed also followed the same equation, though the Langmuir constant had dropped very considerably.

2. *The effect of exchangeable* Ca *and* Al *on soils A, B, and C*

Two pretreatments were compared, washing three times with 0·1 N sodium acetate and washing three times with 1 N NaCl. It was found that the acetate displaced only about one-half as much exchangeable calcium and about one-quarter as much exchangeable aluminium as the chloride did. The third wash with the chloride was almost aluminium free. The effect of removing the calcium and aluminium from soils A and C is fairly small. The effect is much larger for soil B at 240 hours, being a reduction of 38 per cent. though the effect was inappreciable at 2·4 hours, and at 24 hours the NaCl washings had reduced the sorption by 20 per cent. This soil contains much readily acid-soluble aluminium, and it appears that some of this only slowly becomes accessible to the phosphate in solution. With calcium acetate buffer and addition of 5 mg. P as calcium monophosphate instead of the corresponding sodium compounds phosphate sorption by soil D was 40 per cent. higher at pH 5·0, as was to be expected.

3. *The effect of the* pH *of the solution*

The pH of the solution was varied from 2·0 to 5·5, using chloroacetate for 2·0 and 3·5 and acetate for 3·5, 4·5, and 5·5, the ionic strengths being adjusted to 0·085 in all the solutions except those at pH 2·0. There was striking insensitivity of the sorption of phosphate to pH in this soil, providing the ionic strength was maintained equivalent. This independence of sorption on pH in the acid range was confirmed by Bache using

soil D and pH's of 3·0 and 5·0, and Ca acetate or chloroacetate buffers and mono-calcium phosphate, for the sorptions were equal to within 0·01 mg. P from the two buffers when the ionic strengths were equalized. In the subsequent work a pH of 5·5 or 3·5 was used, the former to maintain a low concentration of ferric and aluminium ions, and the latter of ferric ions, in solution.

4. *Aluminium-ion concentration in the equilibrium solution*

This was determined by aluminon (Yardley, 1952) after 24 hours shaking in 0·1 N sodium-acetate buffer. The experiment was made when the soil was shaken with buffer alone as well as with buffer plus 1 mg. P.

TABLE 1

Concentration of Aluminium brought out by the Buffer

(Soil A, 1 g. soil, 1 mg. P, 40 ml. solution. Molarity of Al in solution after 24 hours.)

	pH 3·5	pH 5·5
Buffer alone . . .	$4{\cdot}0\times10^{-4}$	$3{\cdot}6\times10^{-6}$
Buffer+1 mg. P . .	$4{\cdot}0\times10^{-4}$	$\leqslant 8\times10^{-7}$
Conc. of P in buffer in M .	$4{\cdot}0\times10^{-4}$	$4{\cdot}1\times10^{-4}$

Table 1 shows that at pH 3·5 the concentration of aluminium was the same whether phosphate was present or not, but at pH 5·5 the aluminium concentration was reduced at least fourfold by the phosphate to a value on the limit of detection by the aluminon method. It should be noted that the product $[Al]\times[H_2PO_4]$ at pH 3·5 is smaller by a factor of about 30 than that for variscite in the presence of gibbsite at this pH, but at pH 5·5 it is just about the value calculated from the data of Cole and Jackson (1950).

The effect of blocking agents on soil A

Table 2 gives the effect of allowing soil A to sorb different amounts of oxine before being shaken with phosphate. The amount of oxine sorbed by the soil was measured by the difference between the initial amount added in the acetate buffer and that removed in the subsequent washes. As usual 1 g. soil was shaken in 40 ml. 0·1 N acetate buffer at pH 5·5.

Table 2 shows that the soil will take up a very large amount of oxine, and this oxine reduces the amount of phosphate sorbed. But there appear to be many more spots on the soil which can sorb oxine than phosphate, so that after 240 hours shaking, the first 34 γ-mole of oxine sorbed reduced the phosphate sorption by 2 γ-mole, whilst the last 521 γ-mole sorbed (from 114 to 635 γ-mole), only reduced it by 2·9 γ-mole. Hence, although oxine reduces the sorption of phosphate by the soil it is not through any simple mechanism by which each molecule of oxine sorbed sits on a spot that could potentially sorb a phosphate ion, for there are far more oxine-sorbing than phosphate-sorbing spots, and not all phosphate spots are blocked by oxine.

Preliminary experiments with other blocking agents have also shown

TABLE 2

Effect of Amount of Oxine absorbed on the Reduction in Phosphate Retention by Soil A

mg. oxine		*γ-moles oxine absorbed*	*Reduction in P uptake in γ-atoms*			
added	*sorbed*		*2·4 hours*	*24 hours*	*240 hours*	*as γ-atoms per γ-mole oxine sorbed*
5	5	34	0·0	0·5	2·0	0·059
10	9·7	67	1·7	2·9	3·2	0·036
20	16·5	114	3·2	2·9	4·1	0·019
100	92	635	6·6	6·2	7·0	0·0055
500	n.d.	n.d.	6·9	7·0	7·0	n.d.
γ-atoms P sorbed in absence of oxine			12·7	15·8	21·2	..

that pretreating the soil with larger quantities had no greater effect on phosphate sorption than had treatment with 0·1 g. per 1 g. soil. Hence in Table 3, which gives a comparison of the efficacies of different reagents in reducing phosphate sorption, 0·1 g. of each reagent was shaken with 1 g. soil for 2 days, and the surplus washed out with the acetate buffer, before the soil was shaken up with the phosphate. The soil deflocculated in the acetate buffer after sorbing alizarin-S or aluminon, and tended to deflocculate after treatment with alizarin and quinalizarin. In these cases excess blocking agent was washed out with the acetate buffer to which

TABLE 3

The Effect of a Number of Blocking Agents on Reducing the Sorption of Phosphate by Soil A

(0·1 g. block added to 1 g. soil A, 1 mg. P added in 0·1 N acetate buffer, ionic strength 0·085 unit.)

	pH 3·5		pH 5·5	
Time of shaking (hours) . . .	*2·4*	*240*	*2·4*	*240*
P uptake by control soil . . .	0·32	0·74	0·35	0·66
% Reduction in P uptake by 0·1 g. of following blocking agents:				
K ferrocyanide	5	1	0	7
selenious acid	17	11	0	8
quinalizarin*	17	9·5	29	23
oxine	14	12	46	33
cupferron	16	14	40	41
alizarin S	11	20	40	45
aluminon	56	63	63	52

* Only 0·02 g. quinalizarin and alizarin were added because of their limited solubility in alcohol.

Note. Morin had almost exactly the same effect as cupferron, and alizarin as oxine at each pH.

sufficient NaCl had been added to flocculate the soil, but these soils were allowed to deflocculate when the amount of phosphate they sorbed from the acetate buffer was measured.

Two other reagents have been used in addition to those given in Table 3, namely fulvic acid and ammonium fluoride. The experiment with fulvic acid was done exactly as with aluminon, for the treated soils deflocculated in the acetate buffer, except that increasing amounts of a H-fulvic acid suspension were shaken with 1 g. soil. The experiment with NH_4F was done in two ways. In series (1) the soil was first shaken in 0·1 N NH_4F for 2 days, washed with 0·1 N buffered sodium acetate, and then shaken with the same buffer containing 1 mg. P. The results for this series are given in Table 4 as reductions in sorption below that for the untreated soil shaken with the same buffer. In series (2) the treated soil is washed with buffered sodium acetate containing 0·1 N NH_4F and then shaken with this same solution containing 1 mg. P, and the results given in Table 4 are reductions in sorption below that for the untreated soil shaken with 0·1 N sodium acetate containing 0·1 N NH_4Cl and 1 mg. P.

TABLE 4

% Reduction of P Uptake by Soil A due to Pretreatment with Fulvic acid or Ammonium Fluoride

(1 g. soil A, 1 mg. P added, 0·1 N acetate buffer ionic strength 0·085. Absorption by untreated soil as in Table 3.)

	pH 3·5		pH 5·5	
Time of shaking (hours) . . .	2·4	240	2·4	240
Mg. C added as fulvic acid per 1 g. soil:				
6·8	28	27	40	35
13·6	63	39	63	48
27·2	..	..	74	55
Pretreating soil with 0·1 N NH_4F:				
Series (1)	..	..	46	14
Series (2)	..	..	75	46

The fulvic acid results are interesting in that the reduction in increment of the phosphate sorption between 2·4 and 240 hours remains at about 0·10 mg. at each pH and at all quantities of carbon sorbed. The fulvic acid suspension contained about 0·02 mg. P in the ash per 6·8 mg. C, so even if all the phosphate it contained was present as orthophosphate, it would still mean that fulvic acid was a very effective blocking agent at the 13·6 mg. C level. The effect of pretreating with ammonium fluoride and washing out excess fluoride reduces the phosphate sorbed by 0·16 mg. after 2·4 hours, but it loses its efficacy with time, presumably due to hydrolysis of the fluoride block. In the presence of 0·1 N NH_4F the phosphate sorbed at 2·4 hours is reduced from 0·44 to 0·11 mg., and at 240 hours from 0·76 to 0·41 mg., showing a very marked depression on the initial absorption but no effect on the slow sorption.

The behaviour of other soils and clays

Soil B, soil C, and the halloysite clay were tested at pH 5·5 in the same way as soil A, both with sodium-acetate buffer alone and after pretreatment with potassium ferrocyanide or oxine.

TABLE 5

Effect of Blocking Agents on Reducing Phosphate Sorption by Various Soils and Clays

(1 g. soil, 1 mg. P added in 0·1 N Na acetate buffered at pH 5·5.)

	Soil B		*Soil C*		*Halloysite*	
Time of shaking (hours)	*2·4*	*240*	*2·4*	*240*	*2·4*	*240*
mg. P sorbed . .	0·19	0·56	0·51	0·88	0·42	0·65
% reduction in P sorption due to pretreatment with:						
K ferrocyanide . .	63	34	10	6	5	0
Oxine . . .	100	73	57	26	36	31
	Bentonite		*Kaolin*			
mg. P sorbed . .	0·11	0·09	0·015	0·015		

Halloysite is clearly behaving very similarly to soil A, showing about the same magnitude of P sorption and the same reduction due to the blocking reagents. This sorption is presumably due to the halloysite itself, for a preliminary wash with N NaCl did not affect the amount of P sorbed, hence this cannot be due to readily mobile aluminium. Soil B has a weaker and soil C a stronger P sorption at 2·4 hours than soil A, though the slow sorption taking place between 2·4 and 240 hours is not much different at 0·37 compared with 0·31 mg. Kaolin hardly sorbed any phosphate, and bentonite only a little, and this all took place rapidly, there being no slow absorption by either clay.

Effect of treating soil A with two blocking reagents in succession

Soil A was treated with two different blocking agents in succession before being shaken up with phosphate in the pH 5·5 acetate buffer, to check if the reagents were affecting the same or different phosphate-sorbing spots.

In the first group, in which all combinations of K ferrocyanide, oxine, and fulvic acid were used, the oxine and fulvic acid seem to block the same phosphate-sorbing spots, and their use in succession gives no additional reduction in phosphate sorption. On the other hand, though ferrocyanide treatment by itself had no effect on phosphate sorption, yet a pretreatment before the addition of oxine or fulvic acid reduced the slow sorption of phosphate, i.e. that sorbed between 2·4 and 240 hours, without affecting the amount rapidly sorbed. In the second group, alizarin S, which by itself behaved much like oxine or fulvic acid, seemed to block some sorbing spots that fulvic acid and oxine did not block, for the subsequent treatment with fulvic acid reduced the rapid sorption by

TABLE 6

Effect of Successive Applications of Blocking Reagents on Phosphate Sorption by Soil A

(1 g. soil, 1 mg. P added in 0·1 N Na acetate, pH 5·5.)

Time of shaking (hours)	*2·4*	*24*	*240*	*Difference 240–2·4 hours*
mg. P sorbed	0·37	0·48	0·67	0·30
Reduction in P sorption due to pre-treatment with:				
Ferrocyanide (Fer)	0·00	0·01	0·04	0·04
Oxine (Ox)	0·16	0·18	0·20	0·07
Fulvic Acid (Fu)	0·16	0·18	0·24	0·08
Fer+Ox	0·17	0·19	0·34	0·17
Fer+Fu	0·16	0·24	0·31	0·15
Ox+Fer	0·10	0·11	0·14	0·04
Ox+Fu	0·18	0·22	0·26	0·08
Alizarin S (Aliz)	0·16	0·19	0·32	0·16
Aliz+Fu	0·26	0·33	0·44	0·18

Note: Fer+Fer and Fer+Fer+Fer the same as Fer.
Fer+Fer+Ox and Fer+Ox+Ox the same as Fer+Ox.
Ox+Fer+Fer the same as Ox+Fer but with Fer+Ox+Fer the soil sorbed about 0·03 mg. less P than with Ox+Fer.
Ox+Ox the same as Ox.
Fulvic acid: 6·8 mg. C added to 1 gm. soil and excess washed out.

0·10 mg. P, i.e. from 0·21 to 0·11 mg. P at 2·4 hours, without affecting the slow sorption. The table also shows that four treatments, the two with alizarin S and the two with ferrocyanide as the first of two successive treatments, reduce the slow sorption of phosphate by about 50 per cent.

The behaviour of hydrated iron and aluminium oxides to blocking reagents

Samples of hydrated iron and aluminium oxides, prepared as already described, were tested for their power of sorbing phosphate in the same way that the soils were, and some typical results are given in Table 7. The principal points brought out are that the oxides are very powerful sorbers of phosphate, that the effect of pH on the sorption of the goethites, though present, is not large, and that sorption increases with time from 2·4 to 240 hours. The blocking agents are all more effective at 2·4 than at 240 hours presumably due to the blocks being hydrolysed, and in this respect differ completely from their effects on the soil, where their effect was always greater at 240 than 2·4 hours. The absolute efficiencies of these blocking agents was rather low.

The effect of removing free iron and aluminium oxides from the soil

The free iron oxides were removed from the three soils by a method which was essentially that proposed by Deb (1950), in which the soil was treated with sodium hydrosulphite in a mixed sodium acetate-tartrate buffer and surplus ferrous iron was removed by treating the soil with 0·02 N HCl. It was, however, necessary to keep soil A in

TABLE 7

The Sorption of Phosphate by Hydrated Iron and Aluminium Oxides

(0·1 g. block used, 1 mg. P in 40 ml., 0·1 N Na acetate buffer.)

	Goethite (1)				*Goethite (2)*			
pH of buffer	pH 3·5		pH 5·5		pH 3·5		pH 5·5	
Time of shaking (hours)	2·4	240	2·4	240	2·4	240	2·4	240
	0·111 g. oxide taken							
P sorbed by oxide	0·45	0·52	0·37	0·53	0·81	0·95	0·77	0·93
% reduction in P sorption due to treatment with:								
K ferrocyanide	31	4	14	2	74	24	31	15
Oxine	24	0	5	4	26	5	38	15
Aluminon	..	..	73	36	..	..	73	42
Fulvic acid (13 mg. C)	..	..	81	43	..	..	65	37

	at pH 5·5							
	Lepidocrocite		*Cold pptd. iron oxide*		*Bayerite*		*Boehmite*	
Wt. of oxide taken in g.	0·111		0·056		0·098		0·075	
P sorbed by oxide	0·55	0·68	0·80	0·97	0·13	0·30	0·57	0·85
% reduction in P sorption due to treatment with:								
K ferrocyanide	44	19	36	10	0	0	30	14
Oxine	18	1	41	12	0	3	18	13

contact with hydrosulphite for 18 hours at 40° C., since a 1-hour treatment, as recommended by Deb, was found inadequate. This is in agreement with Fripiat and Gastuche's (1952) results on Belgian Congo soils. When this treated soil was simply washed with water and then shaken with sodium-acetate buffer, the phosphate-sorbing power of the soil was increased by the treatment. It was assumed that this was due to mobile aluminium ions, so the treated soil was washed with N NaCl till the solution was free from aluminium. It was found that although washing ten times with 10^{-3} N HCl in N NaCl (Schofield, 1949) removed more aluminium than three washes with N NaCl, the subsequent phosphate-sorbing power of the soil was not affected. The percentages of iron and aluminium removed from these soils were:

	Soil A	*Soil B*	*Soil C*
Fe_2O_3	5·8	3·0	6·0
Al_2O_3	1·3	2·0	1·2

Table 8 shows that this treatment decreases both the sorption at 2·4 hours and the slow sorption between 2·4 and 240 hours, but for none of the soils does it reduce it to zero. Again for soil A, the sorption is the same at pH 3·5 as at pH 5·5. However, if these soils are now treated

with a blocking agent, their power of sorbing phosphate is very much reduced. Alizarin S has prevented soil A sorbing any phosphate at 2·4 hours and reduced it to only 0·07 mg. at 240 hours and oxine has had a similar effect on soil B. Oxine, however, prevented the untreated soil B (Table 5) sorbing any phosphate and all that the hydrosulphite pretreatment has done has been to reduce the slow sorption of the oxine-blocked soil from 0·15 to 0·04 mg. P.

TABLE 8

Effect of Removing free Iron and Aluminium Oxides on the Sorption of Phosphate

(1 g. treated soil, 1 mg. P added in 40 ml. 0·1 N Na acetate buffer.)

	Soil A				*Soil B*		*Soil C*	
pH of buffer .	*3·5*		*5·5*		*5·5*		*5·5*	
Time of shaking (hours) . .	*2·4*	*240*	*2·4*	*240*	*2·4*	*240*	*2·4*	*240*
Sorption by untreated soil .	0·39	0·69	0·37	0·67	0·19	0·55	0·51	0·89
Reduction in sorption by hydrosulphite treatment	0·22	0·33	0·18	0·34	0·11	0·38	0·32	0·48
Sorption by hydrosulphite treated soil . .	0·17	0·36	0·19	0·33	0·08	0·17	0·19	0·41
Reduction in sorption due to pretreatment with 0·1 g. of:								
K ferrocyanide	..	..	−0·02	0·04	0·05	0·13	−0·03	0·04
Oxine . .	..	..	0·12	0·22	0·08	0·13	0·10	0·11
Alizarin S . .	..	..	0·19	0·26	..	..	..	..

Discussion of Results

The effect on phosphate sorption of soil A by no less than twelve blocking agents has been depicted in Tables 3 and 4, and was carried out in order to ascertain whether these agents could be classed into groups of similar behaviour. In Table 3 at pH 3·5 aluminon had the maximum effect, followed by alizarin S, while other reagents were mildly effective. At pH 5·5 there was a greater range of effectiveness, with the ferrocyanide and selenious acid having little effect and cupferron, alizarin S, and aluminon being the most effective. No convincing explanation can be offered for the order into which these reagents fall. Since neither ferrocyanide nor selenious acid had any great effect in reducing the sorption of phosphate, iron hydroxides seem unlikely to play much part, particularly since Cooke (1951) showed selenious acid appeared to be a very effective block for this system. The anions of this acid have about the same size as phosphate ions and would therefore be expected to penetrate into finer interstices than the much larger organic ions, but there is no evidence that ionic size is of any importance. The

presence of the blocking agent on the soil surface reduces the concentration of aluminium ions in the phosphate solution at pH 3·5 appreciably: it was 5×10^{-5} M for the morin-blocked soil after 240 hours shaking. Table 3 also shows that the blocks reduce not only the phosphate sorbed at 2·4 hours but also the increment of phosphate sorption between 2·4 and 240 hours. At pH 5·5 the reduction of the increment is only appreciable for the last three reagents used whilst at pH 3·5 it is only appreciable for aluminon.

Potassium ferrocyanide and oxine as blocking agents

The behaviour of ferrocyanide at pH 5·5 varied from zero or little effect on phosphate sorption by soil A and C and halloysite to an appreciable depression on that by soil B at 2·4 hours (Tables 3 and 5). Even the slow phosphate reaction of the soil was hardly affected. On all soils oxine was a fair blocking agent and in particular it completely inhibited phosphate sorption by soil B at 2·4 hours. With the hydrated iron and aluminium oxides ferrocyanide was, surprisingly, more effective than oxine in suppressing phosphate sorption by lepidocrocite and boehmite and almost or equally so with the other oxides.

The conclusions to be drawn are therefore that ferrocyanide and oxine cannot be used to distinguish between sorption of phosphate by hydrated iron and by hydrated aluminium oxides, and that the behaviour of the soil-blocking reagent complex to phosphate is very different from that of the pure hydrated oxide-blocking reagent complex. In the soil system the blocks reduce both the fast and slow sorptions, whereas in the oxide system they rapidly lose efficiency; and in the soil system ferrocyanide is a very ineffective reagent whilst in the oxide it is at least as effective as oxine. The two systems are, however, similar in having their power to sorb phosphate strongly reduced by pretreatment with fulvic acid, and in behaving very similarly at pH 3·5 and pH 5·5.

Blocking agents causing deflocculation

It is interesting to note that aluminon, alizarin S, and fulvic acid which tended to cause deflocculation of the soils, also caused the greatest reductions in phosphate sorption. Aluminon and alizarin S both contain hydroxyl and an anionic group in ortho positions on a benzene ring. Soil A also showed incipient deflocculation after it had sorbed alizarin or quinalizarin, both of which contain two hydroxyls in the ortho position on a benzene ring, but the effects of these blocks on soils B and C were not tested. These results can be interpreted as showing that if the positive charges on the soil particles due to hydroxyls dissociating from iron oxides are replaced by negative charges due to the dissociation of organic acids, the system is likely to deflocculate in the presence of Na ions in mildly acid solutions. Moreover, from the increase of negative charges on soil particles due to such dissociation it would be expected that anions, in particular phosphate, would be repelled (negative adsorption). Certainly the behaviour of these blocking agents suggests that physico-chemical phenomena as distinct from specific chemical blocking of spots are operating. It would follow from this that any soils which

are deflocculated by humic colloids should be phosphate-fixing soils in this sense, and that any soils showing an appreciable proportion of positively charged spots compared with negatively are likely both to show the property of deflocculation by humic colloids and also phosphate fixation. J. D'Hoore and J. Fripiat (1948) have indeed shown that the Yangambi soil in the Belgian Congo shows the phenomenon of deflocculation by organic matter.

An alternative approach to the problem of the form of the sorbed phosphate has been adopted by R. Scott Russell *et al.* who have shown that for short periods after these soils have sorbed phosphate, most of the latter remained isotopically exchangeable with a P_{32} enriched ortho phosphate solution. At this stage most of the phosphate was presumably sorbed in a monolayer. It should be possible to estimate the strength of binding of such a monolayer by determining the phosphate potential of the treated soil in a standard solution (H. C. Aslyng, 1954) and comparing it with that for definite compounds such as hydroxy-apatite and variscite.

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STUDIES ON THE BASALTIC SOILS OF NORTHERN IRELAND

I. CATION-EXCHANGE PROPERTIES

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Summary

Descriptions and analytical data are given relating to nine basaltic profiles representing soils which have been used in detailed studies on cation-exchange properties and mineralogical constitution of basaltic soils in Northern Ireland.

Three main groups of soils are considered: those with impeded or poor drainage, those with free drainage, and those which have good drainage in the agricultural sense but which show slight signs of mottling in lower horizons. In all three groups of basaltic soils the clay contents and the organic-carbon contents fall appreciably with depth, but the cation-exchange-capacity values do not follow the changes in clay and organic-matter contents. The total cation-exchange capacity in the C or G_{2-3} horizon may be as high as or higher than in the surface horizon. In freely drained profiles the cation-exchange capacity is generally lower in the B horizon than in the A(S) or in the C horizon, and usually in poorly drained profiles the cation-exchange-capacity value is also lowest in the B, G_1, or the A_2–G horizon (due mainly to the fall in organic matter). Exchangeable magnesium forms a considerable percentage (up to about 40 per cent.) of the total cations in the C (or the G_2) horizons of basaltic soils, and values of the order of 20 m.e. exchangeable magnesium per 100 g. soil are recorded for some such horizons where drainage is impeded.

In discussing some of the characteristics of the soils of Northern Ireland, McConaghy (1948) showed that the cation-exchange capacities of the basaltic soils are much higher than the cation-exchange capacities of similarly textured soils derived from other parent materials in the region. The actual values for basaltic soils (35–55 m.e. per cent.) obtained in this work were in general agreement with those obtained in investigations on basaltic soils during 1946–7 by Brown (1951, 1954).

An examination of Brown's data shows that in most of the profiles he studied there was an appreciable fall with depth in the clay contents without a corresponding fall in the cation-exchange capacity. Brown drew attention to the high cation-exchange values throughout the profile and to the high exchangeable-magnesium values found for some of these soils and he compared his results with some quoted by Mitchell and Muir (1937), Glentworth (1944), and Hallsworth *et al.* (1952).

In the present paper data are presented relating to nine soil profiles representative of the soils used in further recent studies on the physical chemical and mineralogical properties of basaltic soils and separates.

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The samples were originally collected and analysed in the course of systematic soil-survey work by the authors. Data relevant to the subject of cation exchange are given in this paper.

Experimental

Profiles were exposed by digging pits to a depth of 2½–3 ft. or to the parent rock. Soil samples were taken in succession from the surface downwards, each sample representing one horizon, each horizon being recognized by colour and/or textural or other changes *in situ*. The soil samples were air-dried in the laboratory, ground, and sieved through a 2-mm. sieve.

Mechanical analysis

Except where otherwise stated, the samples were analysed by the International pipette method using sodium hydroxide as dispersing agent (Robinson, 1933).

Loss on ignition

This is expressed as the percentage loss in weight of oven-dry material after ignition at 700° C. It includes organic matter and combined water.

pH

The pH values were determined using a Cambridge meter with glass-electrode assembly. Mixtures of 10 g. air-dry soil and 25 ml. distilled water were allowed to stand for 24 hours, then stirred before readings were made.

Free carbonate

Free carbonate was determined by the standard calcimeter method (Wright, 1939). None of the samples included in Table 1 contained free carbonate.

Organic carbon

Organic carbon was determined by the wet-combustion method of Walkley and Black (1934).

Exchangeable ions and exchange capacity

Cations were displaced using the neutral N ammonium-acetate method of Schollenberger and Simon (1945). Individual cations were determined spectrographically by the Lundegårdh flame-emission method as described by Mitchell (1948). Calcium values were determined chemically by precipitation as oxalate and titration with standard potassium permanganate. Exchange-capacity values were determined by distillation of absorbed NH_4^+ ions with 2N NaOH.

'*Exchangeable hydrogen*'

The method of Parker (1929) was employed, samples being soaked overnight by covering with N barium acetate at pH 7 in stoppered flasks before leaching, and the 'exchangeable hydrogen' determined by

potentiometric titration of the leachate to pH 7 with standard barium hydroxide.

Soil-Profile Characteristics

The soils which are represented include freely drained (Table 1, nos. 7, 8, 9), moderately well drained (nos. 4, 5, 6), and poorly and very poorly drained series.

Soils with poor or impeded drainage

These are generally found in flat or gently undulating terrain on deep basaltic boulder clay. The profile morphology varies somewhat with degree of water impedance, but the following description is fairly representative of the poorly drained series.

Generalized profile description

Horizon	*Depth (in.)*	*Description*
A	0–6	Clay loam, grey-brown with brown and rusty mottlings and rusty streaks in old root channels; cloddy structure; a few stones; merges into
A–G	6–10	brownish-grey layer, cheesy, with rusty mottling; some stones; roots along cleavage planes; changes sharply to
G 1	10–16	sandy or gravelly clay, stony, yellowish brown with intense mottling: orange, rust, grey, green, and ochre; very few roots; massive structure
G 2	16+	gravelly clay; yellow-brown, strongly mottled; with some stones and a few boulders.

Soils with moderately good drainage

These include most of the drumlin soils derived from relatively unsorted basaltic drift. They are found in undulating and in drumlin country where the slope is not sufficiently steep to hinder the normal use of agricultural equipment. In the agricultural sense these soils have good drainage and indeed they make up a considerable percentage of the arable basaltic soils. The subsoils, however, usually show signs of mottling, especially the lower horizons which remain quite moist even after prolonged droughts.

Generalized profile description

Horizon	*Depth (in.)*	*Description*
S	0–10	Dark chocolate-brown loam, with good crumb structure; roots plentiful; a few stones; changes sharply to
B 2	10–20	yellowish rusty brown clay loam, rather compact; with some stones, many partially weathered; some mottling
C	20+	more sticky gravelly clay, fairly stony; yellowish brown with rusty, orange, green, red, and black mottling.

Soils with free drainage

The freely drained profiles considered in this paper are from fairly deep soils overlying sands and gravels or glacial drift which is less argillaceous than the bulk of the unsorted boulder clays in the basaltic region. They are found in undulating country, mainly on moraines or on shallow drift.

Generalized profile description

Horizon	*Depth (in.)*	*Description*
S	0–12	Medium loam, friable; dark chocolate-brown with excellent crumb structure and plentiful supply of fine roots; changes fairly sharply to
B 3	12–24	bright orange-brown or yellow-brown loamy layer; rather cemented but crumbles under pressure to a friable gravelly loam; some amygdaloidal basalt fragments in different stages of decomposition
C	24+	more moist, gravelly loam; slightly mottled but predominantly rusty brown.

Note. In very deep profiles from areas under cultivation there may be traces of a B_1 layer, bright orange in colour and 'loose' in contrast to the cemented B_3 layer immediately below.

Results of Analysis, and Discussion

Soils with poor or impeded drainage.

These soils (Table 1, nos. 1–3) are usually clays or clay loams with clay contents of about 40 per cent. in the surface and in the A–G or G 1 horizons. The clay contents as determined by the International soda method then fall with increasing profile depth, and the extent of this fall in clay with depth is often much greater than might be expected from textural assessment in the field. Associated with the fall in clay, there is usually an appreciable increase in the 'silt' content and often in the fine-sand fraction. The pH values also increase with depth, to values of 6·6–6·9 at about 2½–3 ft. There is seldom any free calcium carbonate in these soils, except in the surface horizon where agricultural limestone has recently been applied.

Exchangeable ions

The total cation contents are fairly high, ranging from about 30 to 57 m.e. per 100 g. soil. Calcium and 'hydrogen' account for much (85–95 per cent.) of these totals in surface horizons, but for appreciably lower percentages of the totals in lower horizons, due mainly to the substantial increases which occur with depth in exchangeable-magnesium values, and to decreases in exchange acidity. These increases in exchangeable-magnesium values are not associated with increased colloidal contents. In the Carnanee profile (Table 1, no. 1), for example, the clay value was 40 per cent. for the surface horizon, falling to 26·4 per cent. in the layer below 20 in., while organic-carbon values fell from 3·7 per cent. in the surface to 0·2 per cent. below 20 in. Exchangeable-magnesium values were 3·9 m.e. per cent. in the surface, 4·8 m.e. per cent. for the 10–20 in. horizon and 17·9 m.e. per cent. for the horizon below 20 in. Such values are typical of the exchangeable-magnesium trends in imperfectly drained basaltic soil profiles, but where drainage is very poor and extensive gleying is evident in or near the surface, exchangeable magnesium values may be quite high even in the surface horizon.

Similar increases in exchangeable-magnesium values with depth have been recorded by many workers including Mitchell and Muir (1937), Glentworth (1944, 1954), Brown (1951), and McConaghy (1948).

Exchangeable-calcium values do not show any consistent trend like that shown by exchangeable-magnesium values, though the highest values are usually in the lowest horizons recorded—the zones of fluctuating water table. The results shown in Table 1 are certainly not in accord with Brown's (1951) statement that the increase in exchangeable-magnesium contents with increasing depth in basaltic soils is usually accompanied by a fall in exchangeable-calcium values, without appreciable alteration in the total exchangeable cations. In the authors' experience of basaltic soils an appreciable and continuous fall in exchangeable-calcium values with depth is not by any means common except under freely drained conditions where surface lime has recently been applied, or in the freely drained series where hard basalt rock is near the surface. As far as total-exchangeable-cation values are concerned, the results in Table 1 indicate that under certain conditions there may be appreciable alteration with depth in the cation-exchange-capacity values of basaltic soils.

These poorly drained or imperfectly drained basaltic soils usually show a slight fall in the total cation content from the surface to the grey G_1 or the A_2–G layer, probably associated mainly with the fall in organic matter. At greater depths there is an appreciable increase in the cation-exchange capacity despite the fall in clay values and organic-carbon contents.

Soils with free drainage

These are friable loams with about 25 per cent. clay and just over 20 per cent. silt in the surface horizon (Table 1, nos. 7–9). The clay contents fall appreciably with depth to values of less than 12 per cent. in the C horizon though textural assessments in the field often suggest rather higher clay values for the subsoils. Organic-carbon contents are usually over 5 per cent. in the surface horizon. Cation-exchange-capacity values are high—over 40 m.e. per cent.—in the A or S horizon and show a definite fall in the B horizon, rising again in the more moist C horizons to values which are of the same order as those of the surface horizons.

The horizon exhibiting the lowest cation-exchange-capacity values in this series of freely drained basaltic soils is usually rather cemented and compact, and it appears to be similar to the indurated B_3 horizon mentioned by Glentworth (1954) though in Northern Ireland the lowest cation-exchange-capacity values do not appear to be associated necessarily with the lowest clay values, as in the soils described by Glentworth. The exchangeable-magnesium values fall from the A to the B horizon and rise again in passing to the C horizon. The extent of this rise appears to be related closely to the degree of moistness and the extent to which mottling is found in the C horizon.

Soils with moderately good drainage

The clay contents of the surface horizons are usually in the 25–32 per cent. range (Table 1, nos. 4–6) and fall with increasing profile depth, as in the freely drained soils. This fall in clay values is often greater than estimates made from textural assessments in the field. Silt contents increase regularly with depth usually within the range 20–35 per cent.

TABLE I

Characteristics of Some Basaltic Soil Profiles

Profile no.	Drainage	Lab. no.	Horizon Depth (in.)		Description (field)	Mechanical analysis: Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Organic carbon (%)	Loss on ign. (%)	pH	Exchangeable cations (m.e. %): Ca	Mg	K	Na	Mn	H	Sum.*	Ex. Cap. (m.e. %)
1	Fair	Z 111	0–10	A	CL, GrBr. m. rust; cloddy	9·2	27·4	16·9	40·0	3·7	15·6	5·65	18·4	3·9	0·29	0·25	0·10	11·2	34·1	38·3
		112	10–20	G_1	C, BrGr. m. Y and rust, massive	13·8	33·7	14·7	34·0	1·5	11·3	6·20	18·5	4·8	0·21	0·25	0·07	5·4	29·2	31·8
		113	20+	G_2	StC, YBr, int. m: Gn–Y–Gr	11·7	34·4	25·5	26·4	0·2	10·0	6·70	25·9	17·9	3·14	0·38	0·05	3·1	50·5	50·5
2	Poor	Z 114	0–8	A	C, dk. Br., m. rust, cloddy	5·8	17·1	22·1	43·8	3·7	13·9	6·26	38·8	4·2	0·35	0·54	0·04	9·2	53·1	49·9
		115	8–16	G_1	C, GrBr., m, compact; fst	4·3	16·4	20·2	44·3	1·8	10·5	6·56	34·6	4·8	0·17	0·56	0·01	6·7	46·8	47·8
		116	16+	G_2	C, fst, YBr, m: Gr–Gn–Bk	3·2	29·3	36·2	23·9	0·2	8·4	6·66	32·1	13·9	0·13	0·90	0·02	4·3	51·4	52·5
3	Poor	Z 124	0–10	A–G	C, GrBr., m. Br. and rust; cloddy	7·7	14·6	19·0	40·3	4·8	19·2	6·05	27·0	5·0	0·28	0·51	0·02	8·6	41·4	41·5
		125	10–15	A–G	C, BrGr., m. rust, compact, sharp to	9·3	16·6	19·3	43·0	2·6	12·9	6·35	32·1	3·5	0·45	0·64	0·03	5·2	41·9	42·1
		126	15–20	G_2	GrC, YBr., m. ochre, Gr–Gn, &c.	5·0	21·6	27·0	40·7	0·3	8·5	6·87	30·7	5·6	0·17	0·86	0·02	2·8	40·2	43·6
		127	20+	G_3	GrC, YBr, int. m: Gr–Gn	5·6	23·5	31·9	30·6	0·2	8·6	6·95	36·3	10·5	0·14	0·84	0·02	3·1	56·9	57·1
4	Fairly good	Z 243	0–12	S	L, dk. choc. Br., crumb, sharp to	5·2	17·6	21·0	24·6	5·0	22·2	6·26	30·5	3·3	0·53	0·50	0·05	12·0	46·9	46·7
		244	12–20	B	grL, YBr, vsl. m. rust; v. compact	5·5	29·1	30·3	21·4	0·4	13·8	6·42	31·5	9·1	0·24	0·84	0·01	5·9	47·6	47·7
		245	20+	C	StCL, YBr, sl. m. rust: Red–Gn	8·7	34·7	33·9	11·7	0·1	11·3	6·37	24·6	12·4	0·25	0·88	0·01	9·2	47·3	40·5
5	Good	Z 117	0–8	S	L, dk. choc. Br, crumb, merges	4·3	19·0	27·4	32·6	4·6	16·3	5·34	9·0	10·3	0·31	0·63	0·10	26·9	47·2	46·3
		118	8–15	S	L, Br, fst, fy sharp to	5·9	23·5	27·9	28·5	2·8	14·4	5·52	11·0	11·7	0·22	0·54	0·05	23·6	47·1	44·4
		119	15–30	B_2	L, lt. Red–Or; fst	8·9	35·5	28·4	16·6	0·8	11·4	5·74	22·1	13·9	0·36	1·81	0·03	15·0	53·2	53·1
		120	30+	C	StCL, YBr, sl. m: Gr–Gn–Red	10·0	35·1	29·2	13·9	0·4	11·0	6·32	30·8	10·2	0·49	1·33	0·02	8·0	56·8	57·1
6	Fairly good	Z 249	0–9	S	L, Br, fst, crumb, sharp to	8·1	22·6	18·5	28·5	5·5	22·0	5·18	14·2	11·2	0·21	0·48	0·06	20·9	47·1	53·9
		250	9–18	B	grCL, fst, YBr, sl. m.	9·3	36·5	28·5	18·8	0·6	10·3	5·60	18·6	12·0	0·14	0·39	0·02	19·3	50·5	49·9
		251	18+	C	grL, St, some m: Y–Red–Gn	7·8	41·2	29·5	13·0	0·2	11·5	5·78	20·2	19·0	0·15	0·53	0·02	14·8	54·7	54·4
7	Free	Z 233	0–15	S	L, dk. choc. Br, crumb, fy sharp to	3·7	21·2	22·8	26·5	5·5	22·2	5·78	16·7	2·4	0·37	0·45	0·02	20·5	40·4	46·5
		234	15–30	B_2	L, YBrOr, cemented, worm casts	3·6	34·8	28·4	16·3	1·6	14·5	6·18	12·8	1·1	0·20	0·37	0·01	20·0	34·5	34·8
		235	30+	C	CL, OrY, tr, m; platy	6·3	38·0	31·4	10·9	0·5	10·5	5·92	17·9	7·5	0·60	0·60	0·02	19·0	45·6	43·0
8	Free	Z 246	0–15	S	L, dk. choc. Br, crumb, fy sharp to	7·2	22·0	26·8	27·3	5·5	17·2	5·79	22·6	4·1	0·60	0·62	0·07	19·7	47·7	45·3
		247	15–24	B_2	grL, compact, OrBr, merges	11·9	34·0	20·3	21·5	1·6	12·2	6·26	16·7	2·6	0·23	0·34	0·01	10·3	30·2	29·8
		248	24+	C	CL, Br ochre, sl. m: Gr–Gn	10·6	39·6	26·8	11·0	0·5	12·1	6·36	23·6	11·4	0·37	0·96	0·04	10·9	47·3	41·2
9	Free	Z 144	0–11	S	L, choc. Br, crumb, merges	9·0	24·3	23·5	25·4	3·1	13·6	5·19	27·7	8·3	1·69	0·59	0·07	14·7	53·1	55·2
		145	11–19	S	L, Br, fst, fy sharp to	8·5	24·5	22·5	28·3	2·7	10·6	6·20	29·8	8·4	0·41	0·56	0·03	11·0	50·2	47·5
		146	19+	B_2	L, ochre-Br, fst, cemented	8·0	40·0	23·7	17·0	0·1	7·4	6·41	14·9	5·5	0·20	0·40	0·01	8·4	29·4	33·2

C clay, L loam, gr gravelly, St stony, Gr grey, Br brown, Y yellow, Or orange, Gn green, Bk black, choc chocolate, fst a few stones, m mottled, tr trace, lt light, v very, sl slight, fy sharp to fairly sharp change to, int intensive, dk dark.

* Results to nearest $\frac{1}{10}$ m.e.

and the fine-sand contents likewise increase with depth. Organic-carbon values range from about 3·5 to 5 per cent. in the surface horizons and then fall fairly sharply in passing to the B horizon. The total cation contents (and cation-exchange-capacity values) are high throughout the profile, usually rising with depth. This rise may be considered as due mainly to changes with depth in exchangeable-magnesium values as the sums of exchangeable-calcium and so-called 'exchangeable-hydrogen' contents are relatively constant with depth. In profiles which have not had dressings of agricultural lime there is generally some rise in exchangeable calcium with depth. The exchangeable-magnesium values in the C or C–G horizons may approach the values found at corresponding depths in the poorly drained soils.

It may be of interest to record here that the lowest exchangeable-magnesium values encountered in soils of basaltic origin have generally been in the surface layers of shallow profiles (immature or skeletal) developing over basalt rock. Under such conditions drainage is very free and values for exchangeable magnesium may be as low as 1 m.e. per cent. in the A or S horizon, and at the parent rock the value may be as low as 2·5 m.e. per cent. In a few cases a slight fall in exchangeable magnesium with depth has been recorded.

General Discussion

The results of analyses given in Table 1 indicate that some variations may occur with depth in cation-exchange capacity of basaltic soils, and that the quantities of individual exchangeable cations may vary appreciably, but the total exchangeable-cation values remain relatively high within the profile, irrespective of soil type. There is reasonably good agreement between the sum of exchangeable cations determined individually on each sample and the cation-exchange-capacity value. Differences in such values are due to the summation of errors involved in individual cation determinations and to the use of barium-acetate solution in determining 'exchangeable-hydrogen' values, other cation determinations and total-exchange-capacity determinations being made on ammonium-acetate leachates. Changes in clay values with depth are not reflected in changes in cation-exchange capacity. Since the organic-carbon contents fall appreciably from the surface and are relatively small (of the order of 0·3 per cent. in the lower horizons) the high cation-exchange-capacity values of these basaltic soils may be considered as due to

(1) increases in the cation-exchange capacity of the clay with depth in the profile, or
(2) the coarser separates contributing appreciably to the total cation-exchange capacity.

No substantial changes have been found in the cation-exchange capacity of the clays within any of the profiles described, and the coarser separates have all shown an appreciable cation-exchange capacity (McAleese, 1954). While difficulty was experienced at times in obtaining complete dispersion of some basaltic subsoils, the cation-

exchange properties exhibited by coarser separates could not possibly be attributed merely to the presence of undispersed clay in such separates.

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STUDIES ON THE BASALTIC SOILS OF NORTHERN IRELAND

II. CONTRIBUTIONS FROM THE SAND, SILT, AND CLAY SEPARATES TO CATION-EXCHANGE PROPERTIES

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Summary

The cation-exchange capacities of soil separates, isolated by the International soda method and decantation from five basaltic soil profiles were determined by the neutral normal ammonium-acetate method of Schollenberger and Simon. The exchange capacities of the clays ranged from 41 to 60 m.e. per cent. The results suggest the presence of clays of the illitic type. Silt separates were found to have high cation-exchange capacities, sometimes greater than those for corresponding clays. The fine sands also exhibited appreciable exchange capacities, the highest again being found usually in the lowest horizon of the profile. Values as high as 20 m.e. per 100 g. were obtained for some of the coarse sands.

Part of the exchange capacity of the separates greater than 2 μ in effective diameter is undoubtedly due to the presence of some clay contaminant, but the actual silt and sand particles also comprise material with considerable exchange capacity.

Introduction

THE cation-exchange capacity of a soil depends on the nature and on the amount of exchange material which is present, and while it was once thought that this exchange material was wholly colloidal in character, it is now generally accepted that silt and fine-sand fractions may have some cation-exchange capacity. Subsoils from many basaltic soil profiles examined in Northern Ireland in recent years (Brown, 1951, McConaghy and McAleese, 1957) have generally been found to have high cation-exchange capacities (of the order of 35–50 m.e. per cent.) even where the measured clay contents and organic-carbon values were low, and it has certainly seemed probable that the coarser separates of these subsoils make an appreciable contribution to the total cation-exchange capacity. Such an assumption is in harmony with the results recorded by Hosking (1948) for basic igneous soils in Australia and with earlier results given by Joffe and Kunin (1942, 1943).

In this paper an account is given of the separation of mineral-soil fractions from a series of basaltic soil profiles described in an earlier paper (McConaghy and McAleese, 1957), and data are presented showing the cation-exchange capacity of each of these separates.

A major difficulty in isolating the soil separates was to evolve a method which would give an adequate separation of the fractions without

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causing appreciable alteration in exchange materials and hence in the cation-exchange capacity. Some workers have attempted separations by purely physical methods, but the majority have employed chemical dispersion agents in conjunction with physical techniques. Joffe and Kunin (1942), Mukherjee (1944), and Hosking (1948) dispersed the materials less than 2 mm. diameter with ammonium hydroxide and after agitation and sedimentation siphoned off the supernatant liquid to a particular depth after the appropriate time interval. The results quoted in the present paper are for fractions isolated after dispersion with sodium hydroxide. In fractionations of this type there is always the problem of effecting complete separations of individual fractions, for a coarse separate may hold a finer separate so tenaciously that ordinary dispersion methods fail to separate them (Sideri, 1936; Baver, 1948). Inorganic cementing agents may also be present, e.g. oxides of iron, requiring special treatment for their removal prior to mechanical and mineralogical analyses. The evidence presented later in this paper suggests that the cation-exchange capacity values obtained for coarse separates cannot be attributed merely to contamination by fine material, though evidence is available that complete dispersion of some basaltic subsoils is difficult to achieve.

Methods

Five soil profiles, described in an earlier paper (McConaghy and McAleese, 1957), were used in this study. Organic matter was removed by oxidation with 6 per cent. hydrogen peroxide, and the separates were isolated by the International soda method of Robinson (1933). Coarse sand was separated by sieving and other separates (fine sand 0·2–0·02 mm., silt 0·02–0·002 mm., and clay $< 0{\cdot}002$ mm. effective diameter) by sedimentation and decantation until repeated removal gave a clear supernatant liquid. Silt separates isolated in this way were again dispersed with sodium hydroxide in 100 ml. centrifuge tubes and centrifuged to remove any clay still remaining in this separate. The bulk volumes of clay and silt were flocculated with calcium chloride, the flocculated separates treated with dilute hydrochloric acid to remove calcium carbonate, washed free of acid with 85 per cent. alcohol, saturated again with calcium chloride to ensure calcium saturation, washed with neutral 95 per cent. alcohol to remove excess salts, dried in the oven at 80° C., and weighed. The clay separates which dried out in an extremely hard condition were ground to pass a 100-mesh sieve. Part of the sample was treated again with three separate lots of 6 per cent. hydrogen peroxide to ensure complete removal of organic matter. The silt separates dried out in rather brittle condition and readily crumbled under the slightest pressure. Part of each silt separate was also treated with hydrogen peroxide. The silt and clay separates were brought to 50 per cent. relative humidity, using glycerol solutions.

The cation-exchange capacities of the sand separates were determined by the neutral normal ammonium-acetate method of Schollenberger and Simon (1945) and distillation of the ammonium-saturated samples with sodium hydroxide (2 N). In the determination of cation-exchange

capacities of the clay separates and (when high values were observed) of the silt separates, the micro-distillation procedure of Mackenzie (1950) was adopted.

Results and Discussions

The results in Table 1 are the means of duplicate determinations on materials which were treated with peroxide before and after separating individual fractions. There were no significant differences between these results and determinations on fractions which received only one peroxide treatment—before separation.

The exchange capacities of the clay separates are fairly high, ranging from 41 to 62 m.e. per cent., only one sample being below 45 m.e. per cent. There is some tendency for the exchange-capacity values of the clays to rise with depth in profiles with imperfect drainage and to remain relatively constant with depth in profiles having good drainage. The exchange-capacity values of the coarser fractions are surprisingly high, and show interesting trends. The values for silts vary considerably, especially in the surface horizons, but they invariably rise with depth, sometimes to values which are higher than those for the corresponding

TABLE 1

Cation-exchange Capacity of Basaltic-soil Separates

(m.e./100 g. at 50% R.H.)

Profile	*Drainage conditions*	*Depth (in.)*	*Cation-exchange capacity of*			
			Clay (< 2 μ)	*Silt* (2–20 μ)	*Fine sand* (20–200 μ)	*Coarse sand* (> 200 μ)
Carnanee	Fair	0–10	45·1	14·2	16·5	16·3
		10–20	46·4	25·0	18·7	15·1
		Below 20	49·2	40·2	21·2	18·4
Ballyno .	Poor	0–8	50·8	35·7	20·4	18·0
		8–16	51·2	38·6	22·8	20·2
		Below 20	47·8	49·5	23·9	20·5
Rashee I	Good	0–8	51·7	43·9	24·6	19·5
		8–15	52·5	48·3	28·9	13·3
		15–30	50·4	57·0	29·5	15·0
		Below 30	51·8	59·3	31·4	13·0
Glynn Hill	Poor	0–10	51·8	20·5	24·8	13·6
		10–15	52·6	21·6	26·2	10·9
		15–20	60·0	48·0	20·3	16·4
		Below 20	61·9	50·3	24·5	14·4
Beltoy .	Fairly good	0–8	46·0	22·8	21·7	11·0
		8–16	41·4	25·0	19·8	15·7
		Below 16	44·4	41·2	28·7	19·6

clay separates. The rises recorded in the exchange capacity of these silts with depth are often substantial. In the Carnanee profile, for example, the values rose from 14·2 m.e. per cent. in the surface to 40·2 m.e. per cent. at 20 in., and in the Glynn Hill profile the values were 20·5 m.e. per cent. in the surface and 50·3 m.e. per cent. in the horizon below 20 in.

In these profiles drainage was fair or poor, and it is interesting to note that in the Rashee profile, with good drainage, the cation-exchange capacities of the silt separates were appreciably higher in the surface and throughout the profile than corresponding values for the poorly drained profiles. From the available data it is impossible, however, to say whether this is a normal feature, though it is obvious that the increases in cation-exchange-capacity values of the silts with depth are typical.

The fine-sand fractions have appreciable exchange capacities ranging from 16·5 to 24·8 m.e. per cent. in surface horizons, and from 21·2 to 31·4 m.e. per cent. in the C or C–G horizons. The values generally rise slightly with depth in the profile. There is no consistent trend in the cation-exchange capacity of the coarse-sand fractions, but it is worthy of note that some of these values, of the order of 20 m.e. per cent., are nearly as high as those of many medium-textured surface soils derived from non-basaltic materials in Northern Ireland.

Clay minerals of the kaolinitic type have much lower cation-exchange capacities (5–10 m.e. per cent.) than those recorded for the basaltic clays in Table 1, which values are of the same order of magnitude (40–50 m.e. per cent.) as those found for illitic clay minerals (Brindley, 1951). Therefore, considering cation-exchange capacity, these results would imply the clay minerals to be mainly of the illitic type. X-ray analysis (to be published later) however, showed the clay separates to be mixtures of clay minerals, the nature and amount of the individual minerals being closely dependent on the drainage conditions of the profile.

The high cation-exchange capacity of the silts separated from these basaltic profiles can not be due to the presence of organic matter. The samples showing highest cation-exchange capacities are subsoils with very low carbon contents and any organic matter present should have been removed by the peroxide treatments. Peroxide was found to have little effect on the cation-exchange capacity of subsoil separates (McAleese, 1954) and therefore on the exchange sites, though Walker (1948) reported that hydrogen peroxide caused exfoliation of vermiculite. Though part of the cation-exchange capacity of the silts may be due to the presence of undispersed clay 'contaminating' the silts, it is difficult to accept the possibility that an appreciable part of each value is due to the presence of undispersed clay. If large quantities of clay were present in the 'silt' separates these separates would dry out hard like the clay separates and not, as found, in friable condition. Repeated dispersions and isolations of silt separates after reduction by nascent hydrogen liberated up to 5 per cent. extra clay from some of the samples, but there was seldom an appreciable change in the cation-exchange capacity of the remaining silt as a result of such treatments. It is therefore concluded that the silt-sized particles are mainly, though not entirely, silt, and that this silt contributes appreciably to the total cation-exchange capacity of basaltic soils and subsoils.

The values obtained for the coarse- and fine-sand fractions are high, some in the region of 20 m.e. per cent. but Hosking (1948) reported values for some coarse-sand fractions of basaltic origin as high as 47 m.e. per cent. Hosking observed the presence of montmorillonitic clay

TABLE 2

Contribution to Cation-exchange Capacity of Soils by the Soil 'Separates'

Milliequivalents

Profile	*Carnanee*			*Ballyno*			*Rashee I*				*Glynn Hill*				*Beltoy*		
Horizon	*0–10 in.*	*10–20 in.*	*Below 20 in.*	*0–8 in.*	*8–16 in.*	*Below 16 in.*	*0–8 in.*	*8–15 in.*	*15–30 in.*	*Below 30 in.*	*0–10 in.*	*10–15 in.*	*15–20 in.*	*Below 20 in.*	*0–8 in.*	*8–16 in.*	*Below 16 in.*
Contribution from:																	
Coarse sand	1·50	5·81	2·15	1·04	0·87	0·66	0·83	0·78	1·32	1·30	1·05	1·01	0·82	0·81	1·14	2·06	1·59
Fine sand	4·52	6·30	7·29	3·49	3·74	7·00	4·67	6·79	10·47	11·02	3·62	4·35	4·38	5·76	3·65	3·52	5·88
Silt	2·40	3·68	10·25	7·89	7·80	17·92	12·03	13·48	11·19	17·31	3·90	4·17	12·95	16·05	3·94	4·85	10·96
Clay	18·04	15·78	12·99	22·25	22·68	11·42	16·84	14·96	8·37	7·20	20·88	22·62	24·42	18·94	18·49	16·64	14·30
Sum of contributions by mineral matter (m.e./100 g. oven-dry soil)	26·46	31·51	32·68	34·67	35·09	37·00	34·37	36·01	31·35	36·83	29·45	32·15	42·57	41·56	27·22	27·07	32·73
Cation-exchange capacity of soil mineral matter by direct determination (m.e./100 g.)	23·14	26·04	41·43	44·83	36·78	50·02	34·11	37·72	50·58	..	27·75	34·36	39·44	47·88	34·74	27·82	37·68

minerals in these fractions, and this was probably responsible for the very high values he obtained. Carroll (1931–2, 1933–4) has also reported the presence of clay minerals in coarse separates, and Marshall (1935) found as much as 30–35 per cent. montmorillonite in the silt separates and 3 per cent. in the sand separates from three soils which he investigated.

The contributions to the total cation-exchange capacity of the soil by the silt and fine-sand separates (Table 1) are very high in the lowest horizons where the measured clay is low and where silt and sand contents are high. These contributions are illustrated in Table 2. The contributions by individual fractions have been calculated using mechanical-analysis data presented in an earlier paper (McConaghy and McAleese, 1957) and cation-exchange-capacity values are listed for each separate in Table 1. There is usually a fall in the contributions by the clay separates and a substantial rise in the contributions by the silt and fine-sand separates with increasing depth in the profile. The contributions by the coarse-sand fractions are small and do not exceed 8 per cent. of the total values. In most instances, the 'summation' values given in Table 2 agree reasonably well with the cation-exchange-capacity values determined directly on the mineral fractions obtained by treating the soil samples with 15 per cent. H_2O_2 to destroy organic matter. In a few cases there are considerable differences in the values, but this is not surprising as the summation values are subject to all the accumulative errors arising in the individual determinations such as sand, silt, and clay contents and the cation-exchange capacities of each of the separates.

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AFFORESTATION AND SOIL REACTION

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Summary

An investigation is described of the pH relationships between the soil, litter, and tree leaves at ten experimental areas from 17 to 50 years after planting. At each of these areas a number of different tree species has been established.

From the results of 6,900 pH measurements taken in 13 unplanted and 100 forest plots some general relationships in the pH of tree leaves, litter, and soil are recognized. When a number of tree species are grown under identical conditions the acidity of their leaves and litter layers differs considerably between species. Soil pH is modified differentially by afforestation, largely depending upon the nature of the established tree species and for the ten series of plots it has been possible to prepare a list of tree species graded according to their effect on soil pH. Since the results have been obtained from only ten areas the detailed conclusions must be regarded as tentative. It is suggested that there is a need to establish experiments where the influence of tree species on site conditions can be critically studied. The application of these observations to problems of land use is discussed.

Introduction

WOODLANDS occur over approximately 5 per cent. of the land surface of Great Britain, but for Europe as a whole the proportion is much higher at 26 per cent. (Forestry Commission, 1952). In order to increase the woodland area in Great Britain new forests are being planted, but these forests are usually situated, for economic reasons, on 'marginal lands' where soil and climatic factors restrict the number of tree species that can be grown successfully. Under these conditions relatively few indigenous tree species are suitable for commercial forestry and foresters are relying more and more upon exotics for afforestation. Within the last 100 years the area of land planted with introduced species has increased steadily and as the new woodlands mature they are forming a significant feature of the British countryside. On the whole the exotics have been planted as pure, even-aged blocks, but it seems possible that native tree species will later spread into the blocks to form mixed woodlands.

Several ecological factors may be modified by a change in land use, and in view of the unfortunate consequences that have sometimes followed the introduction of exotics, concern has been felt about the possible effects of the new plantations upon the existing flora, fauna, and soil, particularly where the initial soil conditions are poor (Duchaufour, 1953). There is a need to compare the complex relationship between trees and soil in plantations of different exotics at various stages of development grown under a variety of conditions in Great Britain. Ideally the comparison should be made in a series of controlled experimental plots established for this purpose and having a sound statistical basis, but because of the longevity of trees the first assessment must be made in existing forests. Of present-day woodlands, old silvicultural experiments, originally designed to compare the growth of different tree species, have

proved the most suitable and a preliminary investigation of ten of these experiments has been made. Each area includes a number of tree species grown under similar conditions, but unfortunately there is hardly any duplication of individual tree species. Wherever possible, adjacent sites without any tree cover have also been examined.

This account is concerned with the pH of tree leaves, surface humus layers, and the underlying soils in woodlands. Soil pH gives some measure of the general level of fertility (Truog, 1948; Wilde, 1954) so that a comparison of soil pH under different crops may be of value in indicating the direction and rate of change of soil properties induced by different forms of land use (Salisbury, 1922; Pearsall, 1952).

Methods

A preliminary survey was made of a number of forestry research experiments but, because of major topographical or soil variations, some had to be discarded whilst at others the sampling area was restricted. For instance, at one area, Cwm Du, the peat becomes shallower across the silvicultural experiments and sampling was therefore limited to an area in which the peat was more than a metre deep and no tree roots penetrated to the underlying mineral soil.

Depending upon soil variability five or ten profiles were sampled over the main rooting depth in each tree stand. In this investigation the litter derived from the trees was not regarded as soil and was separated into fresh litter (L) and decomposing material (F+H). All soil depths were measured from the base of H and the soil samples were collected at 5 cm. intervals in the top 20 cm. and less frequently throughout the rest of the rooting zone. So far as possible, tree leaves were collected from trees adjacent to the sampling pits. The sampling of each area was accomplished within a few days during the summer months and all areas were sampled between 1950 and 1953 inclusive.

The pH was determined in a 2:1 sample:distilled water mixture using a glass electrode. The interval of time between the collection of samples and pH measurement was constant for each area but varied for different localities, in some cases pH being determined almost immediately after sampling and in others at intervals of up to a week.

Experimental Areas

The ten series of plots are distributed throughout England and Wales as shown in Fig. 1 and the general characteristics of the localities are summarized in Table 1. Bedgebury, Abbotswood, Powis, Olleys Farm, and West Tofts have all been described previously (Ovington, 1953 and 1954*a*), and general descriptions have been given of the Cirencester plots and some of the North Wales localities by James (1951) and Zehetmayer (1954) respectively.

General Relationships

In Fig. 2 the pH of the leaves and their associated litters has been plotted against that of the surface soil as well as against the average soil pH

FIG. 1. The location of sampling areas.

TABLE 1

Locality Description

Locality	*Plantation age (yrs.)*	*Altitude (ft.)*	*Slope*	*Annual rainfall (ins.)*	*Geology*	*Remarks*
Bedgebury	17–22	250	Gentle	33	Hastings Beds	Compact silty clay
Abbotswood	23–46	350	Gentle	40	Old red sandstone	Coarse sandy loam
Cwm Du	26	1,000	Gentle	100	Ordovician shales	Deep sphagnum peat, drained
Beddgelert	24	1,350	Steep	100	Ordovician shales	Exposed situation, washed down detritus
Clocaenog	19	1,450	Gentle	60	..	Thin calluna peat, manured with 2 oz. basic slag/tree.
Powis	23–29	750	Steep	40	Wenlock shale	Grey-brown loam
Gwydyr	*c.* 28	250	Steep	60	Boulder clay	Deep mineral soil
Olleys Farm	24	125	Flat	24	Chalky boulder clay	Freely drained sandy soil
Cirencester	17–50	465	Gentle	35	Oolitic limestone	Shallow soil, cultivated before planting.
West Tofts	20	125	Flat	24	Chalky boulder clay	Freely drained sandy soil

throughout the main rooting zone. The distribution of tree roots down the soil profiles varies considerably, but there is a tendency in woodlands for the finer roots to be concentrated in the upper soil (Scholtes, 1953). It was thought that the pH of the leaves and litters might therefore be more closely correlated with the surface soil than the whole profile, but in fact the correlation coefficients do not show any great difference (Table 2). A broad positive correlation exists between the pH of the soils and those of the tree leaves and litter layers, despite the very wide

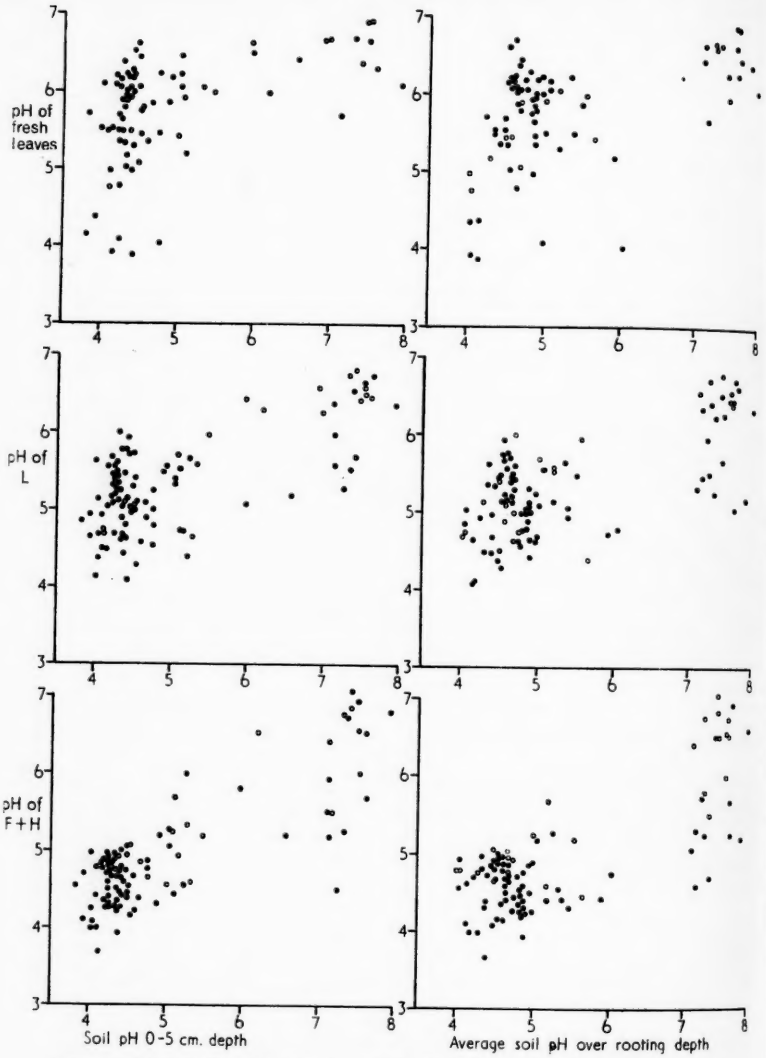

FIG. 2. The relationship between soil pH and the pH of fresh leaves L and F+H horizons.

● Conifers. ○ Hardwoods.

TABLE 2

Correlation Coefficients between the pH of Organic Material and the Underlying Soil for all Plots

	Hardwoods		*Softwoods*	
Soil depth . .	*0–5 cm.*	*0–base*	*0–5 cm.*	*0–base*
Fresh leaves . .	0·89	0·89	0·76	0·80
Litter . . .	0·81	0·85	0·61	0·53
F+H . . .	0·89	0·88	0·71	0·65

range of ecological conditions and woodland types included in the experimental areas. This correlation is more significant for hardwoods than conifers, but the difference may only be a reflection of the smaller number of areas having hardwood stands.

The pH ranges of the leaf and litter layers for any soil pH in Fig. 2 are largely dependent on several variables of which the inherent features of the different sites and of the species planted seem to be of particular importance.

The litters at Cwm Du, for instance, are all less acid than corresponding litters from other areas of similar soil pH, whilst the Abbotswood samples tend to be more acid. This effect is not surprising when it is considered that soils of similar pH may be peats or mineral soils of varying depths and subjected to very different climatic conditions. The samples were also taken in stands of different ages and were collected in different years. Baker and Clapham (1939) have shown that soil pH may vary with the time of sampling.

Although the soils at each locality are broadly similar, the pH values recorded for the leaves and the litter horizons of the various tree species differ considerably. The pH range for the conifer stands is greater and overlaps that of the hardwoods. Some conifers, notably *Chamaecyparis lawsoniana* and *Thuja plicata*, are more comparable to the hardwoods than to conifers such as *Pseudotsuga taxifolia* and *Abies grandis* which have more acid leaves and humus horizons. When the pH values for the fresh litters and the underlying humus are compared, the F+H horizons are more acid than the litter in 68 of the 73 plantations of conifers. In contrast no consistent difference occurs for the 27 hardwood stands where acidity increases with litter decomposition in 14 (approx. half) of the plots.

Effects of Tree Species

Foresters, in selecting research areas having some degree of uniformity, were probably guided by such features as ground vegetation and slope. Unfortunately the variation in soil pH over each area at the time of planting is unknown, but because of the relatively large area required for silvicultural experiments some initial differences would undoubtedly be present. After 20 to 50 years of afforestation the soil pH tends to have a discontinuous variation over each experimental area that can often be related to differences in tree cover.

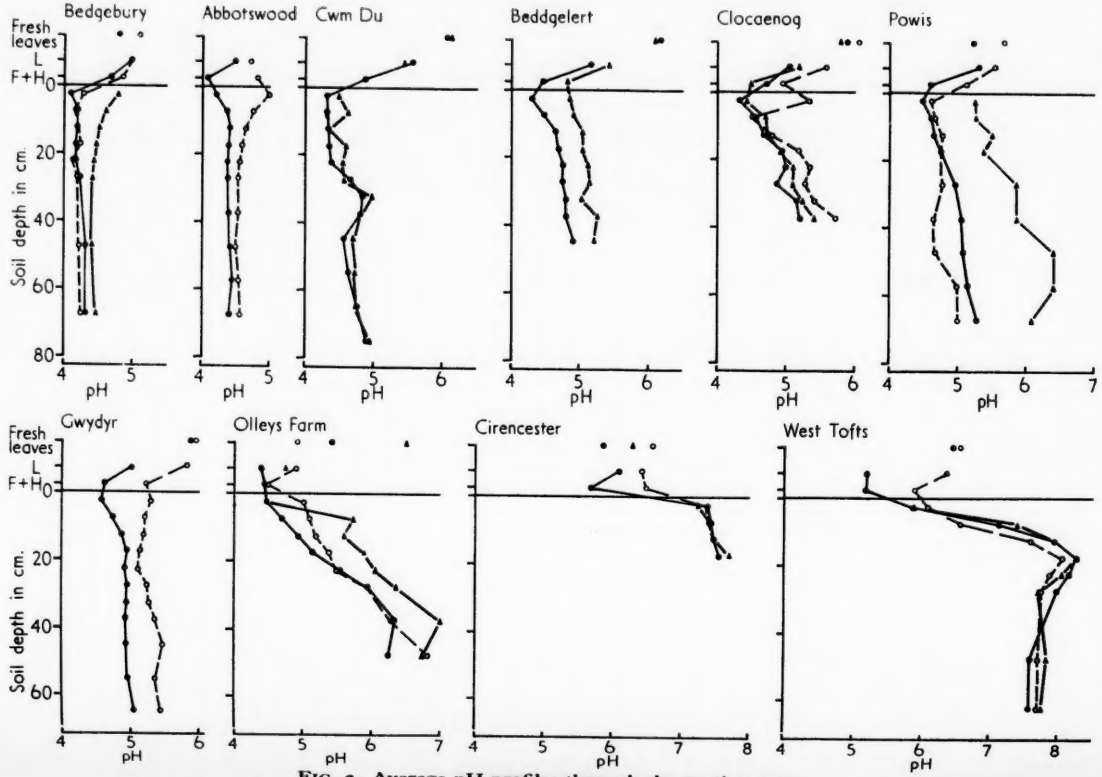

FIG. 3. Average pH profiles through the rooting zone.
▲——▲ Unplanted. ●——● Conifers. ○——○ Hardwoods.

Comparisons of forested and non-forested plots could only be made at 7 localities. At West Tofts and Cirencester, where the soils are alkaline, 12 of the 23 forest plots have an average soil pH less than that of the open, but for the localities having acid soils only 2 of the 43 forest plots have an average greater than that of the corresponding unplanted areas. Since there is no evidence that the allocation of plots was determined by soil conditions prior to planting, the difference between forested and unforested plots would suggest that there has been a relative increase in soil acidity with the afforestation of the acid soils (Table 3).

TABLE 3

The Average pH of the Soil over the Rooting Depth after Periods of Afforestation of up to 50 years

Locality	*Bedge-bury*	*Abbots-wood*	*Cwm Du*	*Beddge-lert*	*Clocae-nog*	*Powis*	*Gwydyr*	*Olleys Farm*	*Ciren-cester*	*West Tofts*
Number of soil profiles sampled in each plot	5	5	5	5	5	5	5	5	10	10
Open	4·51	..	4·67	5·07	4·95	5·72	..	5·97	7·47	7·60
Chamaecyparis lawsoniana and *C. nootkatensis*	4·34	..	..	..	..	..	5·34	..	7·84	..
Thuja plicata	4·34	..	4·68	..	..	..	5·06	..	7·72	..
Fagus sylvatica	..	4·55	..	..	..	4·67	..	..	7·61	..
Larix eurolepis	4·42	..	..	..	..	..	..	..	7·46	..
Picea sitchensis	..	..	4·59	4·68	4·84	5·49	..	..	7·37	..
Quercus spp.	4·27	4·57	..	..	..	4·56	5·00	..	7·64	..
Picea abies	4·23	4·28	4·58	4·80	..	..	..	..	7·29	..
Pinus sylvestris	..	4·48	4·61	..	..	..	..	5·90	7·25	..
Larix leptolepis	..	..	4·58	4·62	..	..	..	6·03	7·18	..
Pinus nigra	4·15	4·40	4·52	..	..	..	4·89	5·39	7·17	7·69
Betula alba	..	..	..	..	..	..	..	5·65	..	7·50
Alnus incana	..	..	..	..	..	..	..	..	7·13	7·30
Abies grandis and *A. nobilis*	..	4·39	4·50	..	..	..	4·86	..	..	..
Pseudotsuga taxifolia	4·05	4·53	..	..	..	4·55	4·85	5·19	..	7·11
Pinus contorta	..	..	..	..	4·76	..	..	5·00	..	..
Tsuga heterophylla	4·04	..	4·48	..	..	..	4·84	5·00	..	..
Larix europaea	..	4·29	..	..	..	4·64	4·76	4·98	..	..

N.B. The forest plots at Clocaenog were slagged when planted.

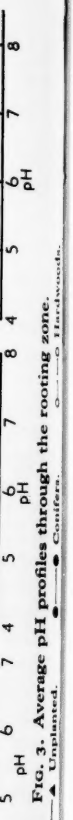

FIG. 3. Average pH profiles through the rooting zone.

Because of natural limits in the potential distribution of trees and the fact that the experiments were set up as independent units no tree species occurs at all ten areas. The lack of duplication of individual species at any locality makes an estimation of the relative effects on soil pH of each tree species difficult, but by considering the ten areas as a group, some tentative conclusions may be drawn.

Seventeen tree species, representing 83 forest plots, occur in more than one area and in Table 3 these tree species and the localities have been graded in order of pH of the underlying soil. When arranged in this way, virtually the same species sequence occurs in nearly all areas. The highest values of soil pH are associated with stands of *Chamaecyparis lawsoniana* and *Thuja plicata*, whilst the most acid soils occur in the plantations of *Pseudotsuga taxifolia*, *Pinus contorta*, *Tsuga heterophylla*, and *Larix europaea*. Soil pH differences reflect differences in leaf composition, for instance, leaves of *Chamaecyparis lawsoniana* compared with *Tsuga heterophylla* are relatively rich in calcium. The consistency in the sequence of species when arranged in order of soil pH suggests that the trees influence soil acidity in distinct ways and the relative effects are similar for the range of localities that has been examined.

The whole soil profile is not modified uniformly, but the intensity and direction of change varies for different soil horizons. The differential effect down the profile probably results from variations in rooting intensity and the leaching of nutrients from the decomposing litter into the surface soil. Since root distribution and litter composition differ considerably between forest stands, the species list arranged with respect to soil pH will vary according to the soil horizon used. For instance, five species occur in at least half of the ten localities, and when they are arranged in order of decreasing soil pH for the whole profile the sequence is *Picea sitchensis*, *Quercus* spp., *Picea abies*, *Pinus nigra*, and *Pseudotsuga taxifolia*, but when the sequence is based on the top 5 cm. of soil it becomes *Quercus* spp., *Picea sitchensis*, *Pinus nigra*, *Pseudotsuga taxifolia*, and *Picea abies*.

Comparisons are often made between hardwoods and conifers as groups, but any differences obtained must, in part, be due to the individual species which happen to be included, since there is a similar range of effects in both groups. Eight of the ten areas studied have both conifer and hardwood stands. When the soil pH figures over the rooting depth are compared the soils associated with the hardwoods as a group are less acid than those under the softwoods in five of the eight areas, whilst at the remaining three localities the reverse is true. For all eight areas the average pH for the soil of the hardwood stands is 5·57 and for the conifers is only slightly less at 5·45.

The type and amounts of the organic layers developed at ground level in the forest plots varies considerably. The pH of the litter horizons is comparable to that of the underlying soil at sites where the soil is relatively acid, but where the underlying soil is alkaline in reaction the litter is more acid than the corresponding soil.

Discussion

The differences of soil pH recorded between woodland and open plots indicates that soil conditions are modified by afforestation, the direction and rate of change depending upon the initial soil properties and the particular tree species that is planted. Once the trees are established the nutrient uptake, nutrient turn-over, and micro-climate vary between plots and the differential effects of trees on soil pH are probably a reflection of this. The pH differences are, however, relatively small and the maximum range of soil pH for the forest stands at each site is usually only about 0·5 pH units but tends to be slightly greater on the more alkaline soils. As a plantation develops into high forest there are associated changes in the ground flora, micro-climate, litter fall, &c. (Chandler, 1941, 1943; Ovington, 1954*b*, 1955; Ovington and Madgwick, 1955), so that the effect on soil pH of establishing a particular tree species may vary throughout the history of the stand. In order to ascertain the progressive change in soil pH it would be necessary to take samples in the same plot over a period of years. From a comparison of the old and young stands it appears that the greatest change in soil pH occurs within the first 25 years after planting. There is no evidence that the change is continuous or intensifies throughout the life of a plantation.

No sharp distinction in their effects on soil pH can be made between natural groupings such as hardwoods and conifers or exotic and indigenous trees and the forester must consider each species individually for afforestation purposes. Where the growth of a tree species of high economic value results in soil deterioration, it may be possible to maintain fertility by growing it in mixture with other species. However, the final evaluation of the effects on soil pH of different tree species planted singly, or in mixtures, depends upon the setting up of more precise experiments and it is of interest that such an area which also includes sheep-grazed plots has been established jointly by the Forestry Commission and the Nature Conservancy at Gisburn in the Pennines. Such investigations may indicate the most satisfactory type of land use for the maintenance of soil fertility.

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ABNORMALITIES IN NUTRIENT UPTAKE BY CORSICAN PINE GROWING ON SAND DUNES

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Summary

Monthly variations in foliar N, K, Ca, Mg, and P_2O_5 of young Corsican pine growing on the sand dunes of Culbin Forest, Morayshire, have been compared with monthly changes in the available moisture in the rooting zone, calculated with the aid of Penman's formula. A reversal of the normal seasonal trends has been observed in the second half of the growing season. In trees showing poor growth, heavy thinning delayed the drying out of the rooting zone and temporarily improved the K, Mg, and N levels in the foliage.

In a previous communication (Wright, 1956), attention was drawn to an apparently abnormal seasonal decrease in the major nutrient content of litter collected from stands of Corsican pine (*Pinus laricio* Poiret) growing on the sand dunes of Culbin Forest, Morayshire, and it was suggested that this might be due to the low levels of soil moisture known to exist in the rooting zone of the trees at the beginning of the growing season. The aim of the present investigation is to determine the time of year at which these fluctuations occur, which of the major nutrient elements are affected, whether they are in fact related to soil moisture, and how far they may be remedied by normal silvicultural methods.

Sampling Areas and Procedure

Culbin Forest has been established, chiefly by recent Forestry Commission planting, on the extensive aeolian sand dunes on the south coast of the Moray Firth. A general description of their origin and topography has been given by Steers (1937), and detailed work on the influence of tree planting on the development of a soil profile was begun by Ovington (1950). In the areas chosen for the present study, the soil consists of an extremely well-sorted quartz-felspar sand with a median grain size of 0·20–0·23 mm.; 90 per cent. of the material lies between size limits of 0·10 and 0·25 mm. The mechanical composition does not vary appreciably with depth, and there is practically no silt or clay present, resulting in low nutrient levels and an extremely low moisture-holding capacity. The water table is far below the rooting depth of the trees, which are therefore entirely dependent for moisture on the relatively low rainfall, which averages approximately 24 in. per annum.

In 1953 the Forestry Commission established two sets of small thinning plots in compartments of pure Corsican pine, one in an area of poor growth (compartment 9) where the trees are below average height, and carry only 2 years' growth of yellowish, rather small needles, and the other in a stand showing normal growth, $\frac{3}{4}$ mile to the south-east (compartment 70). The growth is affected over an extensive area in the neighbourhood of compartment 9; the topography is comparatively flat

and low-lying, resulting in greater liability to frost damage during early spring, and is traversed by numerous shingle bars and fans, the remains of former beach lines, which have the effect of still further reducing the amount of fine material favourable to root development in the total rooting volume of the soil.

The plots were all thinned in 1953, and details of the remaining crop are given in Table 1.

TABLE 1

Crop Measurements in 1953

Compt. no.	*Type of thinning*	*Age (yrs.)*	*Plot size (acres)*	*Length of leading shoot (in.)*	*Stems per acre*	*Top height (ft.)*	*Av. Q.G.* B.H. (in.)*	*Basal† area per acre (sq. ft.)*	*Volume† per acre (cu. ft.)*
9	Light	26	0·5	7	804	25	3¼	59·81	627
9	Medium	26	0·5	5½	548	23	3½	41·60	477
9	Heavy	26	0·5	4½	352	26	3¾	28·67	412
70	Light	27	0·5	10¾	776	27	4¼	89·61	1,234
70	Medium	27	0·5	11	466	27	4¾	71·64	832
70	Heavy	27	0·5	11	444	27	4½	60·44	702

* Quarter-girth, breast height, Hoppus measure. † Hoppus measure.

The thinning grade normally adopted at Culbin is C/D, and corresponds to the 'light' grade in Table 1. The 'heavy' grade is unusually severe for British conditions, approximating to that advocated by Craib (1939), and is intended to eliminate entirely competition between at least the crowns of the trees, although it is doubtful whether even such drastic isolation as this entirely relieves root competition under the dry soil conditions of Culbin, which lead to the formation of unusually extensive root systems.

Needle samples were taken at monthly intervals throughout 1954, from five trees chosen at random each month in each thinning grade, giving a total of thirty samples per month. The samples were obtained by stripping the current year's growth of needles, excluding those near buds, from a lateral branch in the upper third of the canopy on the southern side of the tree. This procedure was adopted to eliminate as far as possible the differences in nutrient content known to occur between needles in different positions on the same tree (White, 1954).

After oven-drying the needles at 80° C., milling, and ashing at 450° C., calcium, potassium, and magnesium were determined spectrographically in 0·1 N HCl extracts (Mitchell, 1948). Phosphate was determined colorimetrically using sodium molybdate, after wet digestion with nitric and perchloric acids, and total nitrogen by the semi-micro-Kjeldahl method of Markham (1942).

Results

(i) *Seasonal fluctuations common to all plots*

The data obtained on the monthly variations in the levels of calcium, potassium, magnesium, nitrogen, and phosphate in the needles are shown graphically in Fig. 1, in which each point represents the mean value from the plots as a whole, i.e. the mean of thirty determinations.

It is generally agreed that, for both hardwoods and conifers, the levels of potassium, nitrogen, and phosphate in the foliage decrease as the growing season progresses, while calcium increases during the same period, magnesium remaining roughly constant (Lutz and Chandler, 1946; Leyton, 1948; McVickar, 1949; Tamm, 1951; Owen, 1954). In the present case, these trends are exactly followed by all the elements

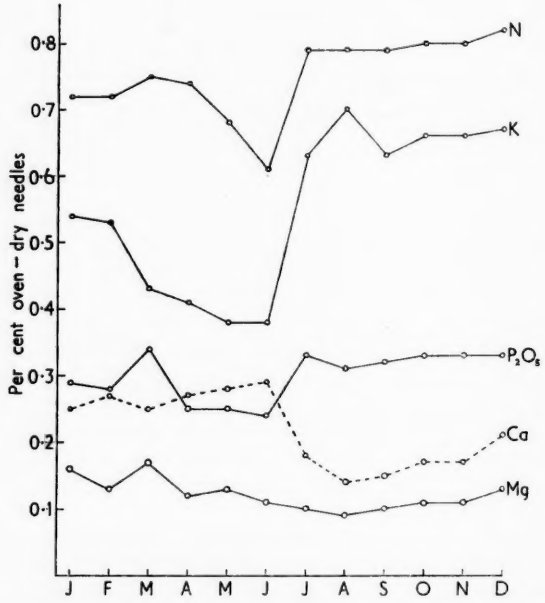

FIG. 1. Monthly fluctuations in nutrient content of the needles.

studied during the first half of the growing season (March–June). During the remainder of the period, however, there is a complete reversal of the normal trend; calcium and magnesium decrease, and nitrogen, phosphate, and potash increase sharply.

(ii) *Differences between plots*

Considering the data for any one month, there are no significant differences between the thinning grades in compartment 70, where growth in general is satisfactory. In compartment 9, where growth is poor, the foliage of the trees in the lightly thinned plot show significantly lower values of potassium and magnesium than the other plots in the month of May only, and of nitrogen in the month of June only. Differences in the levels of calcium and phosphate are not significant in any month. The actual values, expressed as the means of five samples from each plot, are given in Table 2.

TABLE 2

Foliage Nutrient Content in Compartment 9 during the Period April–July, 1954. Per cent. O.D. Needles

	Thinning grade			
	Light	*Medium*	*Heavy*	*5% S.D.*
April:				
K	0·456	0·454	0·416	0·097
Mg	0·118	0·146	0·136	0·037
N	0·712	0·690	0·718	0·070
May:				
K	0·282*	0·376	0·436	0·078
Mg	0·092*	0·134	0·152	0·033
N	0·658	0·682	0·656	0·064
June:				
K	0·434	0·430	0·364	0·093
Mg	0·102	0·122	0·128	0·031
N	0·516*	0·610	0·672	0·074
July:				
K	0·608	0·532	0·580	0·093
Mg	0·094	0·108	0·114	0·029
N	0·792	0·762	0·884	0·187

* Significantly lower than other plots ($P = 0·05$).

(iii) *Correlation with soil moisture*

The results of the leaf analyses show that

(*a*) Foliage nutrient levels are abnormal in all the plots during the latter half of the growing season.

(*b*) In compartment 9, where growth in general is poor, the levels of potassium and magnesium in the lightly thinned plot are lower than those in either the medium or heavy thinning in May, and the level of nitrogen is lower in June.

Since moisture levels in the rooting zone of young trees at Culbin is known to fall to critically low levels during the growing season, and since the most obvious difference between the Culbin site and those on which were observed the 'normal' fluctuations reported in the literature is its low moisture-holding capacity, an attempt has been made to correlate the results of analyses with moisture fluctuations in the rooting zone. These fluctuations were followed by balancing the effective rainfall, i.e. the rainfall actually reaching the soil surface after allowing for interception by the canopy and the forest floor, against the evapo-transpiration calculated on a monthly basis by Penman's formula (Penman, 1949). Data for this calculation were obtained from several Meteorological Office stations in the vicinity of the forest, as follows:

Rainfall and mean air temperature at Findhorn, 3½ miles north-east of the plots.

Vapour pressure and wind speed from Kinloss, 5 miles east.

Duration of sunshine—mean between Nairn, 7 miles south-west, and Forres, 4 miles south-east.

Penman's formula enables the potential evapo-transpiration from vegetation to be obtained from the value of evaporation from an open-water surface (E_0), calculated from the above meteorological data, by multiplying E_0 by a factor which varies slightly during the year from 0·6 in November–February to 0·8 in May–August. This factor has been checked experimentally for grass, and has been applied successfully to sugar beet (Penman, 1952), but has not hitherto been used for trees. The adoption of the same factor for a young conifer crop in close canopy is justified if we consider the *potential* evapo-transpiration, i.e. the maximum possible water loss from vegetation fully supplied with moisture, as the resultant of the balance between incoming and reflected solar radiation, the source of the energy required in the transpiration process. This balance will be affected solely by the ability of the vegetation to reflect solar radiation, and this ability is approximately equal for all vegetation. Differences due to the different transpiration characteristics of different vegetation types only come into play when the moisture supply falls below the optimum.

A mean value for the interception of the rainfall by the canopy, which varies according to the rainfall intensity, was obtained by measuring the rainfall in the plots in compartment 9 during the month of March 1954. Ten small tins were placed at random in the lightly thinned plot, and ten more in the heavily thinned plot. The rainfall collected in these tins was removed and weighed at 24-hour intervals during rainy weather, the tins being replaced in a new position after each determination. The intensity of rainfall in the open during the month varied from 12·4 mm. on the 3rd to 0·2 mm. on the 19th, 20th, and 21st, 77 per cent. of the total rainfall for the month falling in showers of more than 2·5 mm. per day. In the lightly thinned plot, the rainfall reaching the ground surface varied from 52 per cent. of that in the open during a light shower, to 69 per cent. during the heaviest shower. The corresponding figures for the heavily thinned plot were 89 and 93 per cent. The effects of stem-flow and interception by the forest floor were not considered, since recent work on similar crops has shown the former to be small (Hoover *et al.*, 1953; Ovington, 1954), and the sand surface in this compartment is almost entirely free from organic matter.

On this basis, the mean effective rainfall during the year was calculated as being 60 per cent. of the total rainfall in the case of the light thinning, and 90 per cent. under the heavy thinning.

Monthly variations in potential evapo-transpiration and effective rainfall in the two plots, calculated in this way, are shown graphically in Fig. 2. In the calculation of the potential evapo-transpiration, no allowance has been made for the rather lower crown density in the heavily thinned plot; since the evaporation from the sand surface is known to be low (Wright, 1955), the values given will tend to be an over-estimate for this plot.

In order to calculate the moisture balance in the soil, it remains to define the rooting zone. Previous work on trees of the same age, growing on a similar site, showed that although rooting on the dunes was much deeper than on a more normal soil, 92 per cent. of the total root system

lay in the top 3 ft., and similar determinations made in the plots gave values ranging from 87 to 95 per cent. Since the occasional roots which penetrate below 3 ft. are in any case probably primarily concerned with moisture rather than nutrient uptake (Hoover *et al.*, 1953), the effective rooting depth has been taken as 3 ft. Using predetermined values for the field capacity, wilting-point, and bulk density

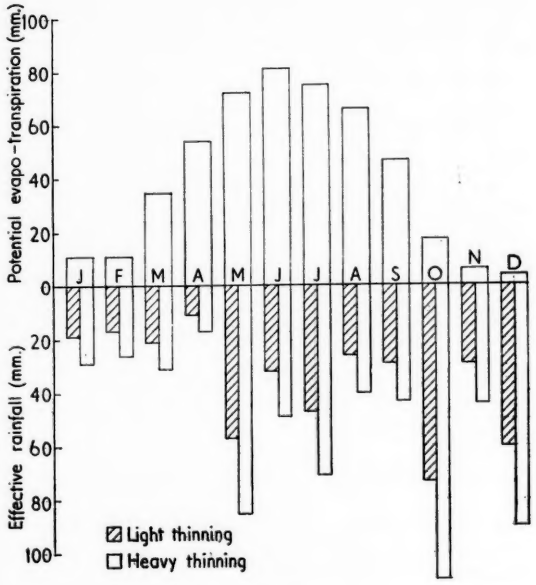

FIG. 2.

of Culbin sand of 5 per cent., 1 per cent., and 1,500 g. per litre respectively (Wright, 1955), the available moisture in this zone at field capacity is equivalent to 60 mm. of rainfall.

The monthly moisture balance in the two plots is shown in Fig. 3.

The values shown in the figure are obtained by adding the algebraic sum of effective rainfall and evapo-transpiration for each plot to the previous month's value for soil-moisture retention. Assuming that the rooting zone is at field capacity at the beginning of January, then, since the effective rainfall in both plots during the month exceeds the potential evapo-transpiration, both remain at field capacity throughout the month, the surplus moisture draining to deeper horizons. The same occurs in February, but by March drainage has ceased, and both plots begin to dry out. In May the rooting zone in the lightly thinned plot dries out to the wilting-point, but the soil under the heavy thinning is still comparatively moist. During the whole of the period June–September the rooting zones of both plots are dry, and are only re-wetted by the autumn and winter rains.

The moisture trends calculated by this method are supported by experimental results obtained in 1952 from a stand of the same age growing on a similar site.

The significant differences in the potassium and magnesium levels in the foliage of the two plots thus occur when the soil in the rooting zone of the lightly thinned plot is at the wilting-point, while that under the

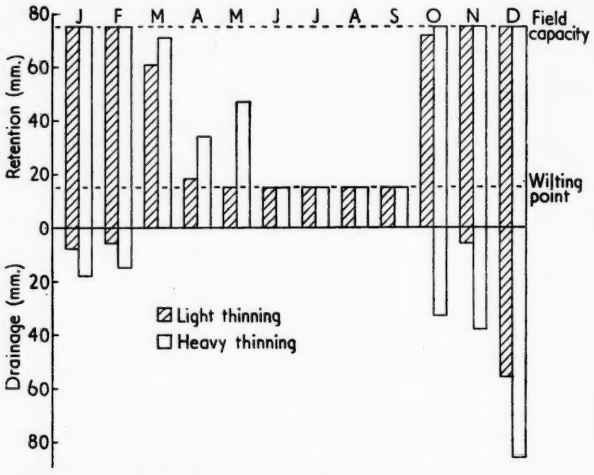

FIG. 3. Compartment 9: monthly soil-moisture balance.

heavy thinning is still moist. No differences were found either when both plots were moist at the beginning of the growing season, or when both had reached the wilting-point. The fact that differences in nitrogen content appeared in the following set of samples suggests that nitrogen uptake may be more affected by previous disturbances in the balance of other nutrients rather than by the direct effects of moisture shortage.

The low moisture levels existing in the latter half of the growing season are sufficiently severe to alter the normal trends of foliage nutrient balance irrespective of thinning grade.

It therefore appears that in areas of the forest where growth is good, typified here by the plots in compartment 70, the adoption of a heavier thinning grade has not yet had any measurable effect on the nutrient status of the trees, but in areas of poor growth the onset of nutrient disturbances may be slightly delayed by heavy thinning; it is too early yet to say whether this will have any appreciable effect on the growth of the crop.

Acknowledgements

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Commission, who gave permission to use the plots and made available the data in Table 1.

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A SIMPLE MONOLITH CONTAINER

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SOIL profiles are normally preserved either as complete monoliths, using, for example, large steel cases of the type described by Clarke (1941) or as frame samples, using the technique of Kubiena (1953). While a large monolith, of course, gives the most complete representation of a soil profile it is extremely laborious to prepare and transport, especially when technical assistance is not available or when the profile pit is on a remote site. Frame samples, on the other hand, although portable and easily prepared, present a discontinuous picture of the profile which is often a grave disadvantage, particularly in collections used primarily for correlation or for teaching.

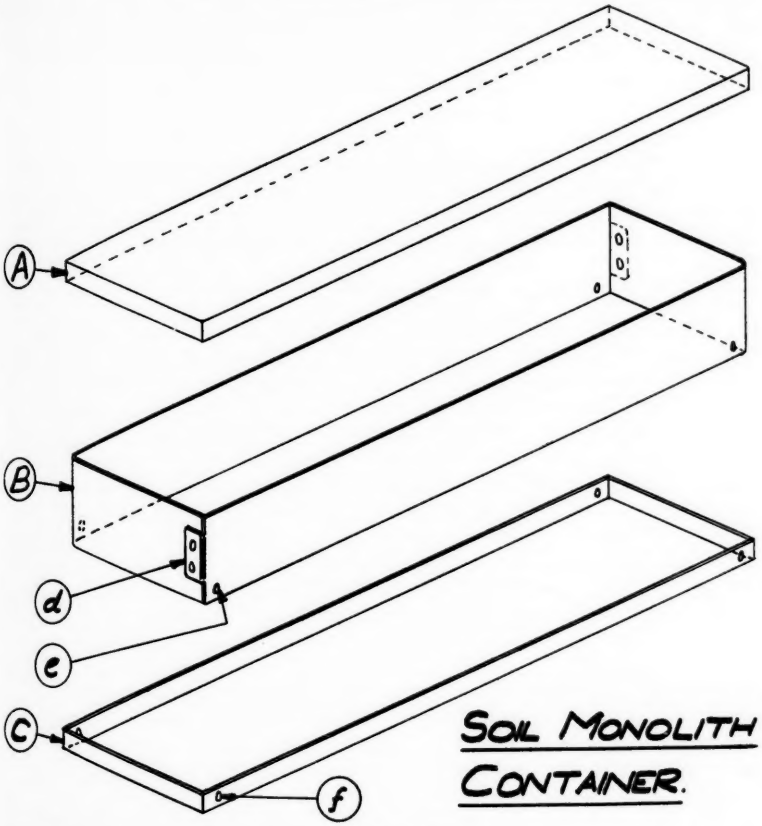
In forming a soils collection at Cambridge the two major difficulties encountered by the author were lack of storage space and of assistance. It was therefore decided to compromise by collecting most of the specimens in short monolith containers of construction similar to that of Kubiena's sample frames and used in the same way.

The container, which is shown isometrically below, consists of an open rectangular box $14 \times 3\frac{3}{8} \times 2$ in. prepared by bending 16-gauge sheet steel, the joints being riveted or tack-welded. (The steel used should be galvanized, lacquered, or otherwise rust-proofed, but aluminium is not recommended as it is too soft as well as unnecessarily expensive.) The box is provided with two close-fitting lids of the same material, the lower one of which is drilled so that it can be secured to the box with four coarse-threaded self-tapping screws in the field.

The container is filled in the same way as a Kubiena frame; the box is placed against the face of the profile pit with its lower lid in place and its long axis vertical and the soil is then cut round with a long knife. After the sample has been introduced into the box, the lower lid is permanently secured with the self-tapping screws, while the upper lid is temporarily fixed with stout rubber bands.

This method of collecting soil monoliths has the following advantages:

1. The sample can easily be obtained by one man using a fairly small profile pit. It takes very little longer to prepare than a frame specimen and may, in fact, save time by taking the place of several frames.
2. Frequently the whole of a soil profile can be accommodated in a single 14 in. container and even a soil 3 ft. 6 in. in depth requires only three. The amount of discontinuity introduced is thus relatively small, except with very deep profiles, such as those of many tropical soils. For such profiles large monolith containers of Clarke's pattern are much more suitable.
3. The dimensions of the containers are such as to allow several to be carried across country in an ordinary haversack. There is, in



A. UPPER COVER. Made in one piece with continuous lip.

B. FRAME. Open both top and bottom, and made in 2 pieces riveted together, internal dimensions $14 \times 3\frac{3}{8} \times 2$ in. deep. Each piece provided with lug *d* bent around for rivets. 4 holes *e* are for fixing screws.

C. BOTTOM COVER. Made as *A* and provided with 4 holes *f*, to match holes in frame, for fixing screws.

addition, room inside each container for five Kubiena frames ($3\frac{1}{4} \times 2\frac{5}{8} \times 1\frac{3}{4}$ in.), which may be required for the preparation of thin-sections to accompany the monoliths in the collection, as well as title-cards, rubber bands, and screws.

4. The prepared monoliths take up relatively little space and can be stored in ordinary drawers or on trays such as are often used for geological collections. They are, moreover, readily portable for class demonstrations, exhibitions, external lectures, or correlation conferences.

A disadvantage of monoliths of any kind is that they give very little idea of lateral variations in soil profiles. It is therefore of the highest importance that each sample in the collection should be accompanied by a good colour photograph of the profile in the field.

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PREPARATION OF THIN SECTIONS OF SOILS

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RECENTLY the author had occasion to prepare a large number of thin sections of soils for micromorphological studies, and it is thought that the experience gained in their preparation and especially in the simplified technique finally evolved might prove of some interest to other workers.

1. *The Problem of Hardening Soils*

Under natural conditions soil horizons vary widely in degree of induration and permeability. Thus in order to prepare thin sections of such materials it is frequently necessary to harden the sample before it is possible to grind it. Any medium used must permeate and harden the soil without altering its natural fabric, and for petrographical studies it should have, ideally, a refractive index of 1·54.

Probably the first material successfully used for hardening friable materials and soils, without disturbing their natural fabrics, was a plastic known as Kollolith (Ross, 1924; Kubiena, 1938). From the method described by Kubiena it appears to suffer from two disadvantages, the necessity of heating to a high temperature (150–70° C.) and the soft grade in which it is supplied commercially. This means that it softens both as a result of frictional heat and from the application of liquids during grinding.

Since many plastics and synthetic resins with characteristics suitable for the preparation of thin sections of soils have recently become available, it was decided to make a comparative study of some of them as hardening and mounting media. For this purpose four contrasting soil horizons were selected—the A and B horizons of a brown earth developed on Devonian limestone from Tornewton, Devon, which would appear to be a terra fusca in Kubiena's (1953) nomenclature; the B horizon of a brown earth of low base status formed on Triassic sandstone from Kenilworth, Warwickshire; and the B_2 horizon of an iron-humus podzol developed on Tertiary sands from Oxshott, Surrey.

Canada balsam, the standby for rock sectioning for many years, was found to be fairly successful both in hardening and mounting, but it deteriorates with age and requires 'cooking' which makes it too brittle to grind easily. Bakelite,[2] both as a lacquer and as a varnish, has been used extensively for hardening materials in America (Leggett, 1928) and a bakelite product available in Britain, SR 17497, has recently been mentioned by Hepple and Burges (1956). This material like Marco Resin SB 28C, used by Alexander and Jackson (1955) for studying soil micro-organisms, has a R.I. considerably higher than 1·54 which is a

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[2] The names and addresses of the firms which supply materials mentioned in the text are included as an Appendix.

disadvantage for petrological studies. Polyvinyl acetate, like bakelite and Marco Resin, can permeate the specimen in the cold, but the grade available is much too soft. Even with repeated impregnations under vacuum, it was not possible to harden the B horizon of brown earths sufficiently to grind. Another material which is too soft for successful hardening is Phoryl resin No. 3. It is useful for mounting, but readily recrystallizes and that at a temperature only slightly higher than its softening-point. This is also the case with Santolite, a plastic which is admirable for hardening types of material that must not be overheated or ground in water (Rowland and Lewis, 1954). Water, however, is a solvent for Santolite, thus care is needed both in the preparation of the sections and in the storage of the slides.

All the soil materials were successfully ground after hardening with dammar gum which is a common gum known to the trade as Dammara. It melts at about 120° C. and is economical since it can be heated repeatedly until becoming badly discoloured without altering its R.I. or strength. Dammar gum does not deteriorate with age, but has a disadvantage in that it is only weakly adhesive to glass and so cannot be used for mounting purposes. In contrast Lakeside 70, a thermoplastic cement made from a combination of waxes, has proved an ideal mounting as well as hardening medium. It has a strong adhesion to glass, softens at 85° C., and successfully permeates clayey soils. Absolute alcohol is recommended as a solvent, but xylene, toluene, or equal proportions of alcohol and acetone may be used instead.

These experiments suggested that the best readily available materials for hardening soils are dammar gum and Lakeside 70, and for mounting Lakeside 70 and Phoryl No. 3. In order to determine whether there was any alteration in the soil fabrics during preparation, a number of soil fragments were polished and compared under a binocular microscope with corresponding thin sections under a petrological microscope. No alteration of the structural morphology of even the highly unstable, iron-stained, colloidal complexes such as are found in fabrics of the B horizons of terra fuscas[1] and braunlehms was observed. The author has made over 200 slides of soils and sediments using these materials, and they have provided a quick and easy method of preparing undisturbed thin sections for micromorphological study.

2. *Method of Preparing Thin Sections of soils*

The preparation of thin sections of soils may be divided into:

(i) Preparation and impregnation.
(ii) Grinding and mounting.

(i) *Preparation and impregnation*

To aid impregnation and to shorten the process of grinding the soil sample should, wherever possible, be carefully cut into a thin tabular form (about 3 by 2 cm.) and 5 to 10 mm. thick. The most suitable equipment to do this is either a small watchmaker's saw or a small

[1] The fabric nomenclature is that of Kubiena (1953).

hacksaw. Most B and C horizons can be prepared in this way, and they then need only one impregnation. Friable and loose horizons cannot be prepared in such a manner and it is often advisable to harden them in the field with polyvinyl acetate. Microstructures are thus retained and the specimens can be prepared in a tabular form in the laboratory prior to impregnation. For fabric examination a useful method is to impregnate a loose sample in a small glass tube, the bottom of which can afterwards be broken and the hardened sample extracted.

To impregnate with dammar gum the prepared specimen is immersed in a dish containing xylene before being transferred to the molten gum. This allows the air to be replaced by the xylene, and in turn the xylene by the hot dammar gum, in the cavities of the specimen. The actual length of time required for hardening varies with the material, but impregnation to a depth of 2 or 3 mm. is sufficient to obtain a hardened, smooth mounting surface. Thus most material will be sufficiently impregnated after 2 to 3 min. If on removing the specimen from the hot gum a thin film of the gum is seen to solidify quickly around the specimen, sufficient impregnation has generally taken place and on cooling the specimen will be hard enough to grind. In the case of a specimen previously prepared in a tabular form the formation of this film on the flat lower surface of the specimen is particularly diagnostic.

With clayey horizons and other material of low permeability the gum, after 2 to 3 min., may still be rapidly filling the interstices in the sample. If this is so, on removal, any gum on its lower surface will not solidify and form a skin, but will be seen to permeate into the specimen. In this case the specimen should be allowed to cool, reimmersed in xylene, and then reimpregnated. It has seldom been found necessary to repeat this process more than once and such a repetition is preferable to leaving such material in the hot gum for a longer period. This safeguards against the overheating of the gum, which can occur if a bunsen and not a hotplate is being used, and against any alteration of the fabric and microstructures within the sample that might well occur under such conditions. If the gum is too hot the edges of the specimen are blackened.

Impregnation with Lakeside 70 is very similar to that with dammar gum. The specimen, presoaked in xylene, is impregnated by heating in a mixture of one part of Lakeside 70 to eight parts of xylene which has been brought to just above melting-point. The mixture is then allowed to boil gently until all the xylene has evaporated when the specimen is removed and allowed to cool.

(ii) *Grinding and mounting*

Thin sections of soils may be ground either with the wet method using carborundum powders or the dry method when sand and emery papers are used. The procedure of grinding with carborundum powders is similar to that employed in making rock slides except that it is not advisable to grind soils in water, since, despite impregnation, the clay minerals swell and the colloids diffuse out. Liquid paraffin, as recommended by Kubiena (1938), is too viscous to allow the abrasives to bite

readily, but kerosene oil allows rapid grinding without loss of part of the colloids. It has also been found that for grinding soil material it is only necessary to use the grades 3F, 600, and the finishing powder Aloxite. Similarly with the dry method, one rough sandpaper for preliminary grinding and the two finest grades of emery paper for finishing are all that are required. With both methods it is essential to prevent mixing the grades of abrasives to avoid scratches, and grinding should in all cases be on individual ground-glass plates.

With either method the first stage is to grind a mounting surface which needs to be finished off with the finest grade of abrasive. The process of mounting is the same whether Phoryl No. 3 or Lakeside 70 is being used, but the latter is preferable. A clean slide is slowly warmed over a bunsen and a small quantity of Lakeside 70 allowed to melt on to the slide. The mounting surface of the specimen is then quickly but firmly pressed on to it. If any air bubbles should be present after mounting they can be quickly removed by rewarming the slide and remounting the specimen. Using Lakeside 70 the slide is ready for the final grinding in one or two minutes.

A great deal of time can be saved from the final grinding if, after mounting, the specimen is cut with a watchmaker's saw or a small hacksaw to a thickness of 2–3 mm. and the rough upper surface smoothed over. The slide should then be gently warmed and the specimen pressed once again on to the slide. This remounting process is very important since it ensures firm adhesion and also brings about further impregnation of the section. When the section starts to become transparent Aloxite or the finest emery paper should be used. The section is now about 0·07 to 0·1 mm. thick, and with the help of a microscope quite large evenly ground sections about 0·03 mm. thick can be produced. After careful brushing and washing the slide is ready for fitting with a cover slip.

It has been found that the best material for mounting the cover slip is Permount. This requires longer to set than liquid Canada balsam, but has the advantage of shrinking less. Permount will set hard in one or two days, but since all dust and extraneous matter are excluded, it is advisable to leave the slide for about a week before finally cleaning it. The surplus Permount on the margins around the cover slip can be removed with a single-edged razor blade and the whole slide wiped with xylene to remove any remaining trace of mounting medium.

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APPENDIX

Names and Addresses of Firms Supplying Materials Mentioned in the Text

Bakelite SR 17497	Supplied by Bakelite Ltd., Redfern Road Works, Tyseley, Birmingham, 11.
Dammara—dammar gum	Supplied by all laboratory suppliers.
Kollolith	Supplied by Voigt and Hochgesang, Göttingen, Germany.
Lakeside 70	Supplied by Hugh Courtright and Co., 7600 Greenwood Ave., Chicago 19, Illinois.
Marco Resin SB 28C	Supplied by Scott Bader and Co., Ltd., Polyester Division, 109, Kingsway, London W.C. 2.
Permount	Supplied by Fisher Scientific Co., Pittsburgh.
Phoryl resin No. 3	Supplied by I.C.I. Nobel Division, 109, Kingsway, London W.C. 2.
Polyvinyl acetate	Supplied by all laboratory suppliers.
Santolite	Supplied by Monsanto Chemicals Ltd., Sales Division, Monsanto House, Victoria St., London S.W. 1.

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